U. S. DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS JOURNAL OF RESEARCH

Vol. 9 NOVEMBER, 1932 No. 5

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BUREAU OF STANDARDS JOURNAL OF RESEARCH

November, 1932
Vol. 9, No. 5

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1932

For sale by the Superintendent of Documents, Washington, D. C. - - Price 25 cents; $2.50 per year on subscription

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THE VARIATION WITH ANGLE OF EMISSION OF THE RADIATION FROM METALS BOMBARDED BY SLOW ELECTRONS

By C. Boeckner

ABSTRACT

The radiation from Pt and W, with its electric vector parallel to the plane of emission, increases rapidly with increasing emission angle. For the other direction of polarization the radiation varies only slowly with angle. The variation is given by the function $(1-R_\theta)/\cos\theta$ where R_θ is the reflection coefficient of the metal for light incident at angle θ. A discussion of the variation of emission from surface layers with angle is given, based on T. C. Fry's theory of lamellar absorption. The disagreement with the observed variation is in the direction to be accounted for if the radiation is initially emitted anisotropically (in a manner similar to the continuous X rays) and is later modified by refraction effects.

It is shown that the angle variation is somewhat similar to that expected for the inverse vectorial photo-electric effect.

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I. INTRODUCTION

There is considerable evidence showing that metals when bombarded by electrons emit visible and ultra-violet radiation. In 1920 Lillienfeld [1] reported a blue gray luminescence appearing at the focal spot of an X-ray tube anticathode, due apparently to the excitation of the metal atoms by the high speed cathode rays. A similar radiation was reported by Foote, Meggers, and Chenault [2] as emanating from a target bombarded by somewhat slower electrons having energies of the order of 1,000 volts.

Recently F. L. Mohler [3] and the author have described a method for studying the radiation from metals bombarded by very slow electrons having energies of from 2 to 15 volts. The method makes use of the fact that a small metal electrode in a gas discharge draws very intense electron currents when maintained at a potential positive to the surrounding space. It was found that with the large current densities thus obtained (4 or 5 amp. cm^{-2}), metals emitted radiation

[1] Lillienfeld and Rother, Phys. Zeits., vol. 21, p. 49, 1920.
[2] Foote, Meggers, and Chenault, J. Opt. Soc. Am., vol. 9, p. 541, 1924.
[3] F. L. Mohler and C. Boeckner, B. S. Jour. Research, vol. 6 (RP297), p. 673, 1931. F. L. Mohler, B. S. Jour. Research, vol. 8 (RP421), p. 357, 1932.

having a continuous spectrum of rather uniform intensity in the visible and ultra-violet.

Some of the characteristics of this radiation are the approximate equality of the absolute intensities from most metals; the exceptional behavior of silver in possessing a very intense emission band in the ultra-violet; and the fact that at low electron velocities the spectrum possesses a high frequency limit in the ultra-violet. It may also be mentioned that the radiation is thought to be the analogue of the continuous X-ray spectrum since the absolute intensity is of the order predicted for the "bremsstrahlung" produced by slow electrons.

The present paper deals with the polarization of the radiation and the variation of intensity with the angle of emission. The measurements were undertaken with the thought that the intensity-angle relation might be similar to that of the continuous X rays. It will be shown later that the velocity of the electrons is normal to the metal surface; it might therefore be expected as in the case of the continuous X rays that the radiation would be most intense when observed in a direction perpendicular to the direction of motion of the electrons. By analogy the radiation might also be expected to be polarized with the electric vector parallel to this direction.

II. METHOD

To study the variation of intensity with angle, a cylindrical electrode was observed in a direction perpendicular to its axis. An enlarged image of the cylinder was focused upon the spectograph slit, the axis of the image being in the plane of the slit and perpendicular to it. From a study of the variation of intensity across the image, information could be deduced concerning the variation of intensity with emission angle. It is clear for example that the radiation forming the edges of the image is emitted at a grazing angle while light at the center is emitted normal to the cylinder surface.

It was thought desirable to study the intensity variation for both the significant directions of polarization of the radiation. A quartz double image prism was therefore placed in the optical train so that one of the images had the electric vector of its radiation parallel to the plane of emission (perpendicular to the cylinder axis) and the other perpendicular to the plane. Since the ultra-violet was found to be the most convenient spectral region for the study of the radiation, quartz fluorite achromatic lenses were used to form the cylinder image upon the slit. It was found necessary to place the double image prism on the source side of the lenses to avoid initial depolarization of the radiation by their quartz components.

A discharge in cæsium vapor (several thousandths millimeter pressure) was used as a source of current to the electrodes for numerous experimental reasons. The cylindrical electrode was placed in the positive column of the discharge coaxial with the cylindrical discharge tube. This arrangement was necessary to secure uniform current density over the electrode surface. The measurements were all made with energies of the bombarding electrons of about 7 volts.

It is of interest to mention that the potential drop between the electrode and the discharge occurs in a small sheath several hundredths of a millimeter thick; the electric force is consequently normal to the metal surface. The direction of motion of the electrons is therefore also perpendicular to the metal surface, since their initial energy

in the discharge is small compared to the potential drop across the sheath.

The metals studied were platinum, tungsten, and silver. The first two metals could be raised to a bright red heat and outgassed by drawing large discharge currents to them while the discharge tube was connected to the pumps. The surfaces were further cleaned by intense ion bombardment.

It was thought of some significance to compare the variation of intensity with angle for a matte surface and a polished surface. A very good diffusely reflecting surface of platinum was prepared by electroplating a layer of platinum black upon a platinum rod and heating to redness in a flame. An attempt was made to prepare a similar tungsten surface by etching a tungsten rod. In this case, however, the surface was far from being a diffuse reflector and showed marked polarization of light reflected from it.

Densitometer records of the blackening across the cylinder image on the spectograms were made by means of a Kip & Zonen registering microphotometer. The intensities were deduced from these records. A series of differently timed exposures on each spectogram served to give the blackening intensity characteristic of the plate. The wavelength range covered was from 4,200 to about 3,100 A.

The method described has the advantage that the intensities for a range of angles may be obtained from one exposure. It has the disadvantage, however, that the radiation emitted at angles greater than 60° to the surface normal correspond to a region so near the edge of the image that results are falsified by errors in focus. The method was, however, found to be convenient and was thought to be adequate for at least a rough survey of the intensity relations. Due to the long exposure times (six hours with the double image prism in place) a more direct method would have been tedious. One set of measurements, however, was made of the intensity of emission from platinum at 75° by comparing the intensity from a large plane electrode observed at an oblique angle with that obtained when observed in a direction perpendicular to the surface.

III. RESULTS

For both platinum and tungsten it was found that the radiation with the electric vector parallel to the plane of emission increased rapidly with the angle of emission (the angle between the emitted ray and the normal to the surface). For the other direction of polarization the intensity was constant across the image. Figure 1 shows a plot of the intensity variation across the tungsten cylinder image, the tungsten being bombarded by 7-volt electrons. The tungsten in this case had been etched in an attempt to render the surface a diffuse reflector. A polished surface, however, gave the same results showing that the intensity is not sensitive to the degree of polish of the surface. There was no appreciable change in variation with angle between 4,200 and 3,100 A.

By drawing large currents to the cylinder, it was possible to heat it to incandescence, enabling measurements to be made of the variation of the intensity of the thermal radiation with angle. For comparison the results are shown on the lower part of the figure.

Figure 2 shows a plot of the intensity-angle variation for polished platinum (full line). The measurements at 75° were obtained from a

large plane electrode which could be observed normally and at an oblique angle. It is seen that in this case the variation with angle changes with wave length. In contrast with tungsten the radiation from the matte platinum surface showed no variation with angle. This is perhaps explained by the fact that the platinum surface is more nearly an ideal diffuse reflector.

Silver showed no variation in intensity across the image of the cylinder. This may, however, be explained by the fact that it was

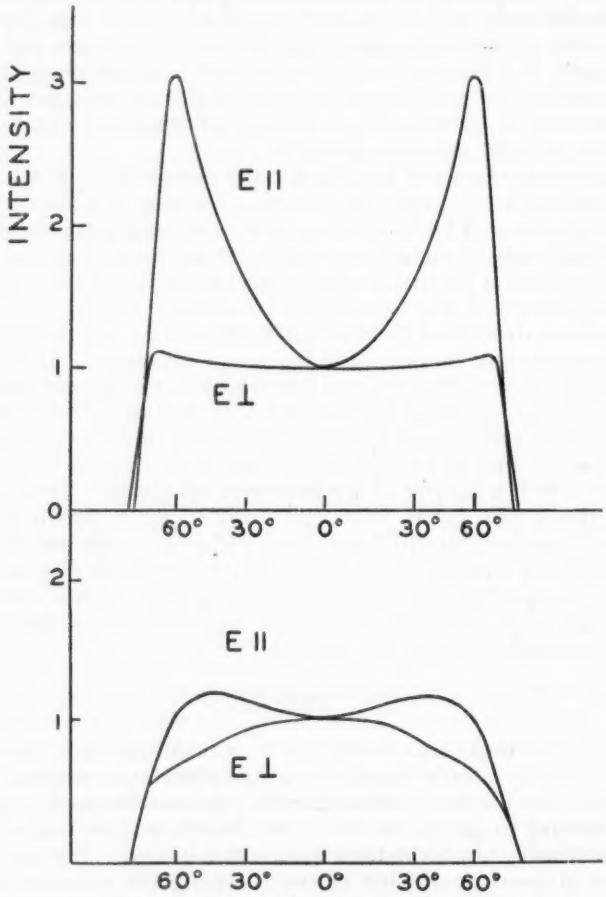

FIGURE 1.—*Intensity variation*

Upper curves, intensity variation across image of tungsten cylinder bombarded by 7-volt electrons. Lower curves, intensity of therma' radiation at 4,200 A

impossible to maintain a polish on the silver electrode in a cæsium discharge, due perhaps to the heating by the large electron currents used.

IV. DISCUSSION

1. RADIATION FROM A THIN LAYER

It is possible to explain the trend of the variation of intensity with angle of emission by assuming that the radiation is emitted by a thin

layer under the metal surface (radiating uniformly in all directions) and is weakened by reflection losses on being transmitted through the surface. The intensity I_θ emitted at angle θ is then given by the relation—

$$I_\theta = \text{constant} \times (1 - R_\theta)/\cos\theta \qquad (1)$$

R_θ is taken to be the reflection coefficient for plane waves incident upon the surface at angle θ. The factor $1/\cos\theta$ arises from the fact that a given area of the image receives radiation from an area of the surface larger in the ratio $1/\cos\theta$.

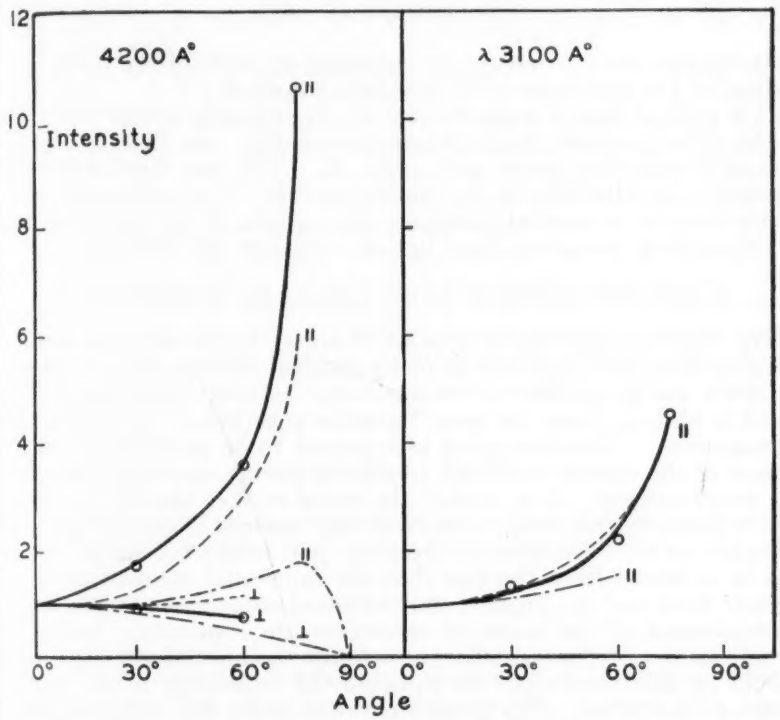

FIGURE 2.—*Variation of intensity with angle of emission of radiation from platinum bombarded by 7-volt electrons, full line*

– – – Plot of $(1-R_\theta)/\cos\theta$
– · – Variation of intensity with angle deduced from the lamellar absorption of platinum.

The dashed lines of Figure 2 are plotted from equation (1). The reflecting powers are computed from the approximation formula given by Drude [4] using the optical constants of platinum given by the International Critical Tables.

The explanation given above is reasonable only if the concepts of rays and the laws of reflection of plane waves can be applied to waves which have a radius of curvature of a few angstroms at the reflecting surface. The latter distance is in all probability the depth from which the radiation is emitted. It is difficult to see, therefore, why the simple considerations used should be correct. A more reasonable

[4] Drude, Ann. d. Phys., vol. 35, p. 523, 1888.

method of estimating the variation of surface emissivity with angle will be given below (relation of surface emission to "lamellar absorption").

2. THE INTENSITY VARIATION OF THERMAL RADIATION WITH ANGLE OF EMISSION

The intensity of the thermal radiation emitted by a square centimeter is proportional to $(1-R_\theta)\cos\theta$.[5] The apparent intensity observed at an angle θ is therefore proportional to $(1—R_\theta)$ or

$$I = \text{constant}\ (1-R_\theta) \tag{2}$$

This relation can be derived by assuming an indefinitely thick layer instead of the thin layer used to obtain equation (1).

It is evident that a measurement of the intensity across the image of the cylinder raised to incandescence enables one to estimate the change of reflecting power with angle, R_θ. This was done in order to estimate the reliability of the measurements. The reflection coefficients relative to normal incidence were about 18 per cent lower at 60° than those computed from optical constants of platinum.

3. SURFACE EMISSION AND "LAMELLAR ABSORPTION"

Fry [6] has discussed the absorption of energy by metal surface layers from incident plane light waves using classical electromagnetic theory. He finds the absorption to be somewhat different from that of the metal in bulk and uses the term "lamellar absorption" to describe the phenomenon. The absorption is supposed to be proportional to the square of the electric intensity (radiation energy density) just under the metal surface. Just outside the metal surface the electric intensity is given by the vector sum of electric vectors of the incident and reflected wave. The electric intensity just inside the metal surface can be obtained from the fact that the tangential component of the electric force and the product of the normal component by the amplitude squared of the index of refraction are continuous across the metal surface. The lamellar absorption computed on this basis should by Kirchhoff's law be equal to the emissivity of the surface layers of the metal. Fry gives a curve showing the variation of the lamellar absorption with angle of incidence of the light for platinum at 4,359 A. The curve should also give directly the variation of intensity of emission with angle and should be directly comparable [7] with the curves of Figure 2. The variation of intensity with angle obtained in this way is not much different from that of thermal radiation, and is therefore not adequate to explain the variation of intensity observed in the present work. If the intensity for normal emission is unity, then at 60° one obtains from the lamellar absorption curves 1.4 for parallel light; for "perpendicular" light, 0.50. The

[5] R. H. Fowler, Statistical Mechanics, p. 493.
[6] T. C. Fry, J. Opt. Soc. Am., vol. 22, p. 307, 1932.
[7] Consider a metal surface in equilibrium with radiation at some temperature and let a suitably defined beam of the radiation with unit cross section area and energy flux I be incident upon a metal surface at angle θ. Let aI be the energy absorbed from the beam by a surface layer of definite thickness. Also let eI be the energy emitted by the surface layer in the direction of the incident beam and from an area of the surface equal to $1/\cos\theta$. Equilibrium between the black body radiation and the surface layer demands that e and a be equal. a as a function of angle can be obtained directly from Fry's work. The units of e, radiation from an area proportional to $1/\cos\theta$, are those used in Figure 2. The curves of Fry for the variation of a with angle for platinum at 4,359 A and those of Figure 2 are therefore directly comparable.

observed values at 4,200 A are 3.6 and 0.77. For comparison the variation of emission with angle deduced from the lamellar absorption is also plotted in Figure 2.

4. RELATION TO THE INVERSE PHOTO-ELECTRIC EFFECT

Another explanation of the angle intensity relations is possible if the phenomenon is correlated with the inverse vectorial photo-electric effect. Relations between the angle variations of the direct and inverse effects can be obtained by considering the conditions to be fulfilled in order that a metal surface be in thermal equilibrium with black body radiation and the thermal electrons in the space about the metal.

The following is a brief discussion based on the "principle of detailed balance." Let Idw be the energy of black body radiation of given frequency passing through unit area, s (perpendicular to the beam), and striking the metal surface at angle θ. The directions of the "rays" in the beam are supposed to be in the solid angle dw. Define P_θ such that $IP_\theta dw$ is the energy absorbed from the beam that is used in ejecting photo-electrons from the metal.

Also let J be the thermal electron current [8] striking unit area of the metal surface and define $i_\theta dw$ such that $i_\theta Jdw$ is the energy emitted by the metal in the solid angle dw as a result of bombardment by the thermal electrons. Then $Ji_\theta dw/\cos\theta$ is the radiant energy from the metal passing through the unit area s. This latter quantity must by the principle of detailed balance equal the energy absorbed photo-electrically from the beam, or

$$Ji_\theta dw/\cos\theta = P_\theta Idw \tag{3}$$

$i_\theta/\cos\theta$ is the apparent intensity of radiation from the surface observed at angle θ; that is, the quantity measured; if we call it i'_θ

$$i'_\theta = cP_\theta \tag{4}$$

where c is independent of angle.

This latter equation implies that the ordinates of Figures 1 and 2 represent also the variation of photo-electric current with angle, P_θ.

The experimental data for the variation of photo-electric current with angle of incidence of the light is rather meager, at least for metals other than the alkalies.[9] For the alkalies the current with the electric vector parallel to the plane of incidence may be from 2 to 10 times greater at 60° than at normal incidence. For the other direction of polarization the current is usually proportional to the incident energy minus that reflected $(1-R_\theta)$. For metals other than the alkalies the increase with angle for "parallel" radiation is much slower. The variation can be expressed by the relations

$$P_\theta\| = \alpha\|(1-R_\theta\|)$$
$$P_\theta\perp = \alpha\perp(1-R_\theta\perp)$$

If α is made unity at normal incidence then $\alpha\|$ at 60° varies from 1 to 2 or 3; $\alpha\perp$ remains closely unity for all angles. It may be mentioned

[8] P_θ should be thought of as referring to the ejection of electrons of some definite velocity and direction and J as the current of electrons having the same velocity and opposite direction.

[9] Photo-electric Phenomena, A. L. Hughes and L. A. Dubridge, McGraw-Hill, 1932.

that $\alpha\| > 1$ is the criterion for the existence of the vectorial photo-electric effect.

If one uses the computed reflecting powers of platinum one obtains from Figure 2 a value for $\alpha\|$ at 60° and 4,200 A of 2.4, for $\alpha\perp$, 1.3; at 3,100 A $\alpha\|$ at 60° is 1.6. These values are not inconsistent with the general trend of the photo-electric measurements.

Ives [10] has successfully explained many phases of the vectorial photo-electric effect for the alkalies by assuming that the photo-electric current is proportional to the lamellar absorbing power of the surface layer emitting the photo-electrons. If this is true for platinum then one would predict for platinum at 4,359 A only a small vectorial effect; that is, $\alpha\| > 1$ and $\alpha\perp$ not much different from unity. The variation of surface emissivity with angle would then be identical with that predicted from the lamellar absorption and would be in conflict with the measurements.

It may be remarked that, if one could use the energy density just above the metal surface instead of that inside as a measure of the absorption or photo-electric current, then one would obtain a very large vectorial effect. If one assumes a gradual transition in energy density between the interior and exterior of the metal, one could explain almost any degree of vectorial effect for the absorption of the first few atom layers. The work of Ives suggests, however, that the discontinuity in energy density is very sharp, occurring within less than an atom diameter.

5. RELATION TO THE VARIATION OF INTENSITY WITH ANGLE OF THE CONTINUOUS X-RAYS

The theory of surface emission given in footnote 7 assumes that the individual atoms radiate uniformly in all directions.[11] The discrepancy between theory and observation may, therefore, be explained by assuming the emitting centers to radiate anisotropically. Such anisotropic radiation is observed for the continuous X rays and is predicted for the radiation from a stream of slow electrons impinging on protons.[12] From analogy to both of these cases the radiation should be most intense when observed in a direction perpendicular to the electron velocity and should be polarized with the electric vector parallel to the direction of motion of the electrons. This is in the right direction to explain the discrepancy since it is found that the "parallel radiation" is much more intense at oblique angles than would be predicted for radiation emitted isotropically. This statement is clear if it is remembered that in the present measurements the electric vector of the "parallel" radiation becomes nearly parallel to the electron velocity at large angles of emission. It is difficult, however, to say quantitatively what should be expected on this view.

In this connection it is of interest to recall the work of Lillienfeld and Rother [13] on the polarization of the visible radiation produced by high speed cathode rays striking a metal target. They observed the polarization for various directions of incidence of the cathode rays and for angles of emission varying from 45° to a very oblique angle.

[10] H. E. Ives and H. B. Briggs, Phys. Rev., vol. 40, p. 802, 1932.

[11] The absorption of a single volume element of the metal is supposed to depend only on the magnitude of the electric vector. This implies that the emission of the element should be independent of direction, its modification by refraction producing the observed angle variation.

[12] A. Sommerfeld, Ann. d. Phys., vol. 11, 257, 1931.

[13] Lillienfeld and Rother, Phys. Zeit., vol. 21, p. 360, 1920.

The radiation was found to be always completely polarized and in the direction to be expected if it were emitted by a classical oscillator vibrating perpendicular to the metal surface. The results can not be explained by a purely optical theory. They suggest, however, that the radiation is produced by the electrons being accelerated through the "work function layer" of the metal. Since such an acceleration is normal to the metal surface, classical electromagnetic theory predicts precisely the type of polarization of the emitted radiation that is observed.

V. SUMMARY

The variation of intensity with angle for both directions of polarization is given approximately by the relation $I(\theta) = (1 - R\theta)/\cos\ \theta$. The equation is obtained by plausibility arguments and has perhaps not a very sound logical basis.

Angle variation based on sounder reasoning (by use of lamellar absorption theory and Kirchhoff's law) fails to explain the facts. The discrepancy may be due either to the incorrectness of the theory or to the fact that the radiation is initially emitted anisotropically as are the continuous X rays.

WASHINGTON, August 3, 1932.

NITROGEN CONTENT OF SOME STANDARD-SAMPLE STEELS

By J. G. Thompson and E. H. Hamilton

ABSTRACT

The nitrogen contents of four Standard Samples of iron and steel have been determined by both the vacuum fusion and solution-distillation (Allen) methods. These four standard samples, with nitrogen contents ranging from 0.005 to 0.028 per cent, are now available as nitrogen standards for analysts interested in this determination.

Repeated analyses of several standard samples of iron and steel showed that the nitrogen content of these samples did not change over periods as long as 13 years.

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I. INTRODUCTION

Studies of various methods for the determination of nitrogen in ferrous materials have been made at the Bureau of Standards for a number of years. Two methods have been commonly used, the vacuum-fusion method and the solution-distillation method, the latter usually referred to as the Allen method. Both methods have been described in detail in previous publications from the Bureau of Standards [1] [2] and in the recent book by Lundell, Hoffman, and Bright.[3] These and other methods for the determination of nitrogen in steel were summarized in a recent publication [4] by one of the present authors.

II. THE USE OF STANDARD SAMPLES OF IRON AND STEEL AS NITROGEN STANDARDS

During the investigation of methods for the determination of nitrogen, Bureau of Standards standard samples Nos. 8b, 23, and 55 have been in intermittent use as reference standards over periods of from 9 to 13 years. Samples 8b and 23 are Bessemer steels containing 0.1 and 0.8 per cent carbon, respectively; sample 55 is an ingot iron. The uniform and reproducible results recorded in Table 1, show that these three standard samples constitute satisfactory reference standards for the determination of nitrogen. A question might be raised as to the stability or permanence of the nitrides present in irons and steels but it is evident, from the data in Table 1, that the nitrogen content of these samples did not change with time during approximately 10 years.

[1] L. Jordan and F. E. Swindells, Gases in Metals. I. The Determination of Combined Nitrogen in Iron and Steel and the Change in Form of Nitrogen by Heat Treatment, B. S. Sci. Paper No. 457, 1922.
[2] H. C. Vacher and L. Jordan, The Determination of Oxygen and Nitrogen in Irons and Steels by the Vacuum Fusion Method, B. S. Jour. Research, vol. 7 (RP346), August, 1931.
[3] G. E. F. Lundell, J. I. Hoffman, and H. A. Bright, Chemical Analysis of Iron and Steel, John Wiley & Sons (Inc.), 1931.
[4] J. G. Thompson, Determination of Oxygen, Nitrogen, and Hydrogen in Steel, Am. Inst. Min. & Met. Eng., Tech. Pub. No. 466, 1932.

III. THE NITROGEN CONTENT OF FOUR CURRENT STANDARD SAMPLES

The available supply of two of these three samples has been exhausted. In order that nitrogen standards may be readily available to workers interested in this determination, the nitrogen content of some of the current standard samples was determined. Four standard samples, No. 10d (Bessemer steel, 0.4 per cent C); No. 55 (ingot iron); No. 101 ("18–8" chromium-nickel stainless steel); and No. 106 (nitriding steel) were chosen, representing different types of iron and steel with different nitrogen contents. Nos. 10d and 55 represent the older, simpler types of ferrous materials with low or medium nitrogen content. Nos. 101 and 106 represent newer types of steel, with medium or high nitrogen content, in which more importance may be attached to the presence of nitrogen. Determinations of nitrogen by both the Allen method and the vacuum-fusion method show that sample No. 10d contains 0.008 per cent; No. 55, 0.005 per cent; No. 101, 0.028 per cent; and No. 106, 0.009 per cent, as recorded in Table 2.

TABLE 1.—*Permanence of the nitrogen content of Bureau of Standards standard samples*

No. 8b		No. 23		No. 55	
Year of analysis	Nitrogen	Year of analysis	Nitrogen	Year of analysis	Nitrogen
	Per cent		*Per cent*		*Per cent*
1919	0.012	1922	0.010	1923	0.005
	.011		.010		.005
	.011		.010		.004
	.011		.010		.005
	.012		.010	1925	.004
1927	.011		.011	1931	.005
	.012		.011		.005
	.011		.012		[1].004
1928	.011		.012	1932	[1].005
	.012		.012		[1].005
	.012	1932	[1].010		
	.013		[1].011		
	.013		[1].010		
1932	.012				
	[1].011				
	[1].010				
	[1].012				
	[1].011				

[1] Determinations made by the vacuum-fusion method. All other determinations were made by the Allen method.

Attention is called to the fact that certain precautions must be observed in order to obtain satisfactory results in the analysis of the nitriding steel, No. 106, by the vacuum-fusion method. The nitrides in this steel are decomposed more slowly in the vacuum-fusion method than are the nitrides of plain carbon steels, and it is necessary to continue the extraction of gases from the sample somewhat longer than usual, in order to insure complete recovery of nitrogen. If this precaution is observed complete recovery of nitrogen is secured, as is indicated by the agreement between the results from the two methods of analysis recorded in Table 2.

TABLE 2.—*Nitrogen content of current standard samples*

No. 10d nitrogen	No. 55 nitrogen	No. 101 nitrogen	No. 106 nitrogen	No. 10d nitrogen	No. 55 nitrogen	No. 101 nitrogen	No. 106 nitrogen
Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
[1] 0.008	[1] 0.004	[1] 0.028	[1] 0.009	0.008	0.005	0.028	[1] 0.009
[1].008	[1].005	[1].028	[1].011	.009	.005	.028	[1].009
[1].009	[1].005	[1].028	[1].010	.008	.005	.028	.010
[1].009	[1].005	[1].028	[1].008	.008		.027	.010
[1].009	.005	[1].028	[1].010			.028	.009
[1].008	.004	[1].026	[1].008				.009
.008	.005	.028	[1].007				.010
.008	.004	.027	[1].009				.010
				Average .008	.005	.028	.009

[1] Determinations made by the vacuum-fusion method. Remaining determinations made by the Allen method.

In view of the numerous requests, which have been received for material to be used as reference standards in the determination of both oxygen and nitrogen, it is unfortunate that these standard samples can not be used as reference standards for oxygen as well as for nitrogen in the vacuum-fusion method. The standard samples are prepared in the form of small, uniform millings, and experience has shown that such samples yield values much too high in the determination of oxygen by the vacuum-fusion method. During the milling process the surface of each chip becomes coated with a thin film of oxide, especially if the chips become heated. In addition to this oxide film, water is usually present as a result of condensation or adsorption during handling and storage. The actual amount of oxygen in the oxide or moisture film on any one chip is very small, but the total from a large number of chips may equal or even exceed the amount of oxygen present in the solid metal of the sample. It is impossible to distinguish between "surface oxygen" and "dissolved oxygen" in the vacuum-fusion method. Consequently, solid specimens with small surface area and correspondingly small contents of "surface oxygen" are preferred for the vacuum-fusion determination of oxygen. The presence of these surface films does not, however, interfere with the determination of nitrogen, and these standard samples are therefore available as nitrogen standards.

WASHINGTON, July 18, 1932.

ANALYTICAL METHODS FOR THE DETERMINATION OF LEVULOSE IN CRUDE PRODUCTS

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ABSTRACT

In sequel to a previous article (RP426) detailed descriptions are presented of analytical methods for the determination of levulose in crude products. The polysaccharides in which levulose is the predominating sugar can be hydrolyzed for analytical purposes in 35 minutes at 80° C. by 0.14 *N* HCl. After hydrolysis levulose is determined either by the selective copper reduction method or by polarization at two temperatures. The volume of the marc from a 50-g sample of artichokes is found to be 0.8 ml. Rapid methods of titrating reducing sugars in low concentration are suggested in extension of the standard methods of Lane and Eynon. Methods of determining the purity of crude and purified juices are described. Applications of the methods of analysis are made to honey and fruits in most of which levulose is found to be the predominating sugar.

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I. INTRODUCTORY

The wide distribution of levulose in natural and manufactured products makes desirable the formulation of a system of analysis for

its quantitative determination. In a previous article [1] some of the fundamental physical properties of pure levulose in aqueous solution and improved methods for its selective determination in sugar mixtures were described. In the present article we shall discuss the determination of levulose in crude natural products and particularly in the intermediate products obtained during the process of preparation of levulose from natural sources by the method described by Jackson, Silsbee, and Proffitt. [2]

In natural products levulose occurs in the form of the uncombined sugar or combined in the form of compound sugars or of polysaccharides. When it occurs as the free sugar it is invariably accompanied by dextrose and frequently by sucrose or other sugar. The polysaccharides which contain levulose have properties which make a direct determination of them at present impossible. They are, however, very easily hydrolyzed by dilute acids and may be determined indirectly by analysis of the products of hydrolysis. The reducing sugars formed by hydrolysis consist of levulose mixed with varying proportions of dextrose. The problems involved in analyzing sugar mixtures containing levulose become mainly questions of differentiation between levulose and dextrose since they practically always occur together.

It will be convenient to characterize these mixtures according to the ratio of levulose to total reducing sugar. Various methods of determining this ratio have been described in the previous article. It can be determined rigorously only by direct analysis for reducing sugar and selective analysis for levulose. In the former article a proximate method was described and designated the Mathews formula (RP426, p. 433) in which it was shown that the ratio could be determined conveniently by combining the direct polarization with the titration for total reducing sugar under the assumption that no optically active substances other than dextrose and levulose were present in the mixture. The Mathews ratio will sometimes be found valuable even when it differs from the true ratio, for the difference then becomes a measure of the optically active or reducing materials which are neither dextrose nor levulose.

In previous articles [3] it has been shown that inulin yields upon acid hydrolysis about 5 per cent of a group of nonreducing difructose anhydrides which are of such high stability as to survive the hydrolysis. No analytical method has as yet been devised to determine these substances directly, since it is impossible to hydrolyze them without employing acid of such high concentration as to destroy the reducing sugar in the sample. In the analysis of juices of plants which contain inulin or similar polysaccharides these refractory disaccharides will escape detection under the ordinary procedure. If, however, we assume that they are mainly responsible for the deviations of the Mathews ratio from the true ratio under the assumption that levulose, dextrose, and the disaccharides are the only optically active substances present, we have a means of determining them approximately.

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[1] Jackson and Mathews, B. S. Jour. Research, vol. 8 (RP426), p. 403, 1932. Repeated reference will be made to Research Paper No. 426 which for brevity will be designated (RP426).

[2] B. S. Sci. Paper No. 519, vol. 20, p. 604, 1926.

[3] Jackson and Goergen, B. S. Jour. Research, vol. 3 (RP79), p. 27, 1929. Jackson and McDonald, B. S. Jour. Research, vol. 5 (RP251), p. 1151, 1930; vol. 6 (RP299), p. 709, 1931.

II. HYDROLYSIS OF POLYSACCHARIDES IN ARTICHOKE JUICES

The juices contained in the roots of the Jerusalem artichoke, dahlia, chicory, and many other composite flowering plants are rich in polysaccharides in which levulose is the predominating sugar. In order to analyze these juices the conditions of acidity, temperature, and time must be found which will yield complete hydrolysis without destruction of the products of the reaction. The experiments described below were performed with the juices and pulp of the Jerusalem artichoke, but the conclusions are equally applicable to any juice or material which contains similar polysaccharides.

In order to determine the proper conditions for hydrolysis weighed quantities of the expressed juice or comminuted pulp of Jerusalem artichokes were introduced into 200 ml Soxhlet flasks, diluted to about 175 ml, and acidified with 3 or 4 ml of 8 *N* HCl. The flasks were immersed in a water bath maintained at either 70° or 80° C. and after selected intervals of time were one by one removed and the contents cooled rapidly. To simplify the procedure the solutions were allowed to assume the temperature of the bath without agitation.

TABLE 1.—*Hydrolysis of artichoke pulp with hydrochloric acid*

(3 or 4 ml of 8 *N* HCl added to 175 ml of solution)

(*a*) 10-g SAMPLE, 4 ml HCl, 80° C.

Time of hydrolysis	Reducing sugars	Levulose	Ratio: $\frac{\text{levulose}}{\text{reducing sugar}}$	Mathews ratio: $\frac{\text{levulose}}{\text{reducing sugar}}$
Minutes	*Per cent*	*Per cent*	*Per cent*	*Per cent*
10	16.74			
20	17.00			
30	17.20	12.45	72.4	67.9
40	17.14	12.43	72.5	68.8
60	17.36	12.53	72.2	67.4

(*b*) 10-g SAMPLE, 4 ml HCl, 70° C.

19	16.90			
30	17.06			
42	17.10	12.45	72.8	70.8
50	17.11	12.23	71.5	70.3
60	17.16	12.54	73.1	69.5

(*c*) 50-g SAMPLE, 4 ml HCl, 80° C.

20	17.20			
30	17.20	12.80	74.4	71.9
41	17.30	12.72	73.5	71.2
52	17.36	12.71	73.2	70.9
63	17.38	12.69	73.0	69.8

(*d*) 50-g SAMPLE, 4 ml HCl, 70° C.

Time of hydrolysis	Reducing sugars	Levulose	Ratio: $\frac{\text{levulose}}{\text{reducing sugar}}$	Mathews ratio: $\frac{\text{levulose}}{\text{reducing sugar}}$
Minutes	*Per cent*	*Per cent*	*Per cent*	*Per cent*
20	17.25			
30	17.28			
40	17.26	12.64	73.2	72.1
50	17.23	12.84	74.5	72.5
70	17.18	12.90	75.1	72.6

(*e*) 50-g SAMPLE, 4 ml HCl, 80° C.

7	11.29			84.0
20	17.10	14.43	84.4	84.1
30	17.04	14.30	83.9	83.7
60	16.96	14.16	83.5	82.4
90	17.19	14.39	83.7	80.7

(*f*) 50-g SAMPLE, 3 ml HCl, 80° C.

10	14.44			82.9
20	17.30	14.86	85.9	83.7
30	17.31	14.64	84.6	83.9
60	17.41	14.61	83.9	83.9
90	17.42	14.65	84.1	83.1

The samples of pulp were prepared by passing artichoke tubers through a food chopper, the plate of which had perforations 2 mm in diameter. The hydrolysis experiments were conducted with 10-g and with 50-g samples. Ten grams is a sufficient quantity if the sugar analysis is made solely by copper reduction methods, while a 50-g sample is preferable if the procedure includes a polariscopic

determination. In the series here described all samples, including the 10-g samples, were polarized, analyzed for total reducing sugar by Lane and Eynon's volumetric method, and selectively analyzed for levulose by Jackson and Mathews's modification of Nyns's method (RP426, p. 425).

The samples after cooling were neutralized and defecated with a saturated solution of normal lead acetate. The addition of alkali was made slowly and with agitation vigorous enough to obviate momentary local alkalinity. The solutions were finally made to volume and filtered. The filtrates were polarized in a 400-mm tube and an aliquot volume was analyzed for total reducing sugar and levulose.

The experimental results are shown in Table 1. Upon examination of the individual series it becomes apparent that regardless of changed conditions of hydrolysis the respective samples arrive at approximately constant compositions after relatively short periods of time. Even when the time is greatly extended there is no evidence of decomposition of the products of hydrolysis. Indeed, in many instances there appears to be a slight increase in total sugar, possibly by gradual hydrolysis of the difructose anhydrides. Table 1(f) shows that 3 ml of HCl is about as effective as the 4 ml used in the other experiments and produces complete hydrolysis in about the same period of time. This can be explained by the fact that the determining factor is the time required to attain the bath temperature and that the hydrolysis itself proceeds very rapidly in either concentration of acid.

The deviations from constancy of the individual determinations are in many cases greater than the experimental error of analysis. These errors arise probably from the difficulty of obtaining complete concentration equilibrium between the solution and the suspended pulp. The divergences diminish, as shown in Table 2, when samples of press juice are hydrolyzed for periods of time between 25 and 60 minutes, although here again there is evidence of gradual hydrolysis of the disaccharides.

The Mathews ratio given in the last column of the tables will be discussed in a later paragraph.

On account of the relative uniformity of all the experimental results the selection of specifications is in a measure arbitrary. Although the hydrolysis can be completed rapidly at 70°, the defecation and filtration of solutions hydrolyzed at 80° were more satisfactory.

Evidently 3 ml of 8 *N* HCl affords sufficient acidity for the samples under investigation. Conceivably samples of greater dry substance concentration might by buffer action greatly diminish the converting power of the hydrochloric acid. The juices upon which the experiments were made contained by refractometric estimation 17 to 20 per cent dry substance. A 50-g sample therefore contained 8.5 to 10 g of total solids. In order to ascertain how great a variation in dry substance can be tolerated, further experiments were made on a press juice in which the hydrolysis was effected by 3 ml of 8 *N* HCl for 30 minutes at 80° C., while the weight of sample was varied from 50 to 160 g. In Table 3 are shown the polariscopic readings of the samples diluted after hydrolysis to a uniform concentration. The solutions containing 50 g and 80 g showed identical polarizations, and the one containing 100 g of sample showed but slightly lower polarization. The experiments indicate that the conditions selected for hydrolysis are

valid even if the dry substance is increased nearly 100 per cent. Such a range of concentrations is great enough for the analysis of all naturally occurring juices, or more specifically, for samples which contain not in excess of 19 g of dry substance. In case of uncertainty the volume of 8 *N* HCl can safely be increased to 4 ml.

TABLE 2.—*Hydrolysis of artichoke press juice with hydrochloric acid*

(50 g juice, 4 ml 8 *N* HCl, 80° C.)

Time of hydrolysis	Reducing sugars	Levulose	Ratio: $\frac{\text{levulose}}{\text{reducing sugar}}$	Mathews ratio: $\frac{\text{levulose}}{\text{reducing sugar}}$
Minutes	*Per cent*	*Per cent*	*Per cent*	*Per cent*
10	17.73	15.25	86.0	82.4
25	17.78	15.26	85.8	82.6
40	17.82	15.25	85.8	82.7
60	17.83	15.33	86.0	82.7
90	17.91	15.38	85.9	82.7

TABLE 3.—*Buffer action of artichoke juice, 19.8 brix*

(3 ml 8 *N* HCl, 30 minutes, 80° C.)

Weight of press juice	Polarization at concentration 25 g per 100 ml ×(−1)	Relative hydrolysis
g	*°S.*	*Per cent*
50	35.7	100.0
80	35.7	100.0
100	35.6	99.7
125	30.9	86.7
160	18.9	52.9

III. ACCESSORY DATA

1. VOLUME OF MARC AND LEAD PRECIPITATE

When a 50-g sample of pulped artichokes has been digested and defecated in preparation for analysis the residual marc and lead precipitate appear very voluminous. To determine the total volume displaced a sample was hydrolyzed and defecated in a weighed and calibrated 200-ml flask and the total mixture weighed after being made to volume. After thorough mixing, a small "catch" sample, about 25 to 30 g, was weighed, made to 200 ml, and filtered. The remainder of the sample was filtered and a 25.00-ml aliquot sample made to 200 ml. The latter and the filtrate from the weighed out sample were titrated in triplicate for total reducing sugar.

If F is Lane and Eynon's factor, T and T' the titers, respectively, of the aliquot and the "catch" sample, V the calibrated volume of the 200-ml flask, v the volume of the marc and precipitate, W the total weight of the hydrolyzed and defecated sample made to 200 ml, and w the weight of the "catch" sample, then

$$\frac{FV(V-v)}{25T}=\frac{F\left(V-\frac{vw}{W}\right)W}{T'w} \qquad (1)$$

in which both terms express the total sugar in 50 g of the sample. All quantities are directly observed except v.

Two determinations yielded the values 0.802 and 0.856 ml for the volume of the marc and precipitate, the difference being within the error of analysis. We shall accept the value 0.8 ml for the marc of a 50-g sample. The volume of the marc of a 10-g sample will therefore be about 0.2 ml.

It is of interest to compare this value with the volume of the marc from the hot water digestion of the sugar beet. A 26-g sample of the latter defecated with basic lead acetate yields a volume of 0.6 ml, while a similar sample of artichoke pulp would occupy a volume of 0.43 ml.

2. THE MATHEWS FORMULA

In the previous article (RP426, p. 433) a formula was derived for the calculation of the ratio (R) of levulose to total sugar in pure mixtures from the direct polarization and Lane and Eynon titration. This formula states that

$$R = f\left(\frac{PT}{D}\right) \tag{2}$$

in which P is the direct polarization, T the corrected Lane and Eynon titer, and D the number of volumes to which one volume of the solution polarized is diluted for titration. A graphic solution of the function yielded a single table from which all values of R could be read o interpolated.

The Mathews ratio has been compared with the true ratio in all products which have been analyzed during the present investigation. In some instances because the measurements required for its solution can be made with higher precision, it has proved more serviceable than the ratio determined rigorously. In other instances a considerable discrepancy has appeared.

The discrepancy between the two ratios is significant, for it becomes an indication of the presence of optically active or of reducing substances which are not levulose or dextrose. In special cases the specific rotations of substances accompanying levulose and dextrose in natural products are known and can be employed for quantitative estimation. Thus, if c is the saccharimetric normal weight (derived from the inverse ratio of the specific rotations of sucrose and of the substance in question), V the volume in which g grams of the sample was dissolved for polarization, T the Lane and Eynon titer, D the number of volumes to which one volume of the solution polarized was diluted for titration, and ΔR the difference between the true ratio and the Mathews ratio

$$\frac{VcD\Delta R}{100gT} = \text{per cent optical impurity} \tag{3}$$

In many natural products it is not to be expected that the formula yields an accurate measure of a definite substance. It is rather a measure of all substances which are not dextrose or levulose, arbitrarily grouped together and estimated as a definite substance which is known to be present, but can not be selectively determined. Applications of the Mathews formula will be made in the analyses reported below.

3. TITRATION OF REDUCING SUGAR IN LOW CONCENTRATION

The convenience and precision of Lane and Eynon's volumetric procedure [4] suggest the desirability of extending the range of concentrations of sugar to greater dilutions in order to permit the rapid analysis of sweet waters, exhausted pulp from the diffusion battery, and, in general, any solution of low sugar concentration. Since at the end of Lane and Eynon's titration the concentration of cupric copper is very small, it is evident that the sharpness of the end point is independent of the initial concentration of copper. We can therefore take for titration smaller concentrations of copper than Lane and Eynon specified for their standard methods and still expect the same definiteness of end point, bearing in mind, however, that the slight excess of sugar required to reduce the methylene blue becomes an increasingly large proportion of the total titer as the amount of copper is diminished. It is consequently essential that the volume of indicator be constant for both standardization and analysis.

Lane and Eynon have shown that 5 ml of the alkaline tartrate constituent of Soxhlet's solution is sufficient to keep the cupric copper in solution even for titrations as great as 50 ml. This concentration of tartrate has been retained in the following experiments. The copper solution has been diminished to 2.5 ml and to 1.0 ml, respectively, and water added to make the total volume 10 ml.

The success of the method depends more upon the skill of the analyst than in the case of the standard methods. In order to perceive the end point more precisely we have altered the standard procedure of Lane and Eynon. Ten milliliters of the mixed dilute Soxhlet reagent was transfered to a 150-ml flask. Somewhat less than the total volume of the sugar solution required to reduce the copper was added, and the flask being held with wooden tongs, the reaction mixture was brought to boiling during continuous agitation over a low free flame. Boiling was continued for one-half minute, the indicator was added, and the titration completed in the usual manner. This procedure permits a close perception of the end point.

The titrations against the solutions containing 2.5 ml of copper solution proved to be about as reproducible as those by the standard methods. The factors for varying ratios of levulose to total sugar and varying titers are given in Table 4. The analyst should always standardize his own procedure by titration of a known solution. The deviation of the factor from the tabulated factor found by experiment can safely be considered constant throughout the table.

TABLE 4.—*Lane and Eynon factors for 10-ml Soxhlet solution composed of 2.5 ml copper-sulphate solution, 2.5 ml water, and 5 ml alkaline tartrate*

(Indicator, 1 drop of 1 per cent methylene blue)

Titer \ R	Dextrose 0	10	20	30	40	Invert sugar 50	60	70	80	90	Levulose 100
ml											
15	26.2	26.3	26.4	26.5	26.6	26.8	26.9	27.0	27.1	27.2	27.3
20	26.4	26.5	26.6	26.7	26.8	26.9	27.0	27.1	27.2	27.3	27.4
25	26.5	26.6	26.7	26.9	27.0	27.1	27.2	27.3	27.4	27.5	27.6
30	26.7	26.8	26.9	27.0	27.1	27.2	27.3	27.4	27.5	27.7	27.8
40	27.0	27.1	27.2	27.3	27.4	27.5	27.7	27.8	27.9	28.0	28.1
50	27.3	27.4	27.5	27.6	27.8	27.9	28.0	28.1	28.2	28.3	28.4

$F=25.74+0.0317\ T+0.0107\ R$, in which T is titer, and R the ratio of levulose to total sugar expressed in per cent.

[4] J. Soc. Chem. Ind., vol. 42, p. 32, 1923.

The titrations against Soxhlet solutions containing 1 ml of copper-sulphate solution were, as expected, less reproducible than those against the standard Soxhlet solutions. The method can, however, be relied upon probably within 1 or 2 per cent of the quantity measured. Within the errors of titration the factor proved to be sensibly constant for variations of sugar concentration and composition. The mean of 7 titrations (indicator, 1 drop of 0.2 per cent methylene blue) yielded a value of the factor of 11.7.

The employment of solutions containing 2.5 ml of copper sulphate in the Soxhlet solution permits the titration of solutions containing from 55 to 180 mg of hexoses per 100 ml. Soxhlet solutions containing 1.0 ml of copper cover a range of 23 to 78 mg in 100 ml.

4. STEFFEN'S REAGENTS

Many of the intermediate products encountered in the production of levulose by the levulate process require a determination of alkalinity expressed as CaO. For this purpose it is convenient to employ the Steffen reagents which are used in the beet-sugar industry. One milliliter of these solutions which are 1.786 *N* is equivalent to 0.05 g CaO. Steffen's HNO_3 and NaOH are suitable for the determination of total CaO by the usual method. To these are added hydrochloric acid and potassium oxalate of the same normality. For convenience they also are called Steffen's reagents and are useful for the neutralization and removal of calcium in the preparation of samples for sugar analysis. These solutions are all of equivalent concentration and consequently the amount of CaC_2O_4. H_2O which is precipitated is related definitely to the volume of Steffen's reagents added. For each milliliter of Steffen's reagent 0.13 g of calcium oxalate is precipitated, and if the density of the precipitate is considered 2.05 [5] the volume displaced is 0.064 ml. The product of 0.064 and the volume of Steffen's oxalate added is the volume displaced by the precipitate.

Calcium oxalate is occasionally difficult to separate by filtration when precipitated from cold solutions. For removing both calcium and lead a mixture of 77.8 g of K_2HPO_4 and 82.2 g of $K_2C_2O_4$. H_2O made to 1 liter is particularly satisfactory. This mixture has the same total normality as Steffen's reagents. The mean density of the precipitate is 2.19,[6] and the volume of precipitate from 1 ml of reagent is 0.065 ml.

The volume displaced by the calcium precipitate can be calculated and deducted from the volume of the volumetric flask. It simplifies the subsequent calculation, however, to add by means of a graduated pipette a volume of water above the mark of the flask equal to the volume of the precipitate. This procedure is adopted for the methods suggested below.

IV. ANALYTICAL PROCEDURE

1. ARTICHOKES OR SIMILAR PRODUCTS

The total reducing sugar in these products can be determined by Lane and Eynon titration and the levulose either by the modified Nyns method or by polarization at two temperatures.

[5] Calculated from data in Handbook of Chemistry and Physics, 13th ed. Chemical Bulletin Publishing Co., p. 190, 1928.
[6] See footnote 5.

(a) PREPARATION AND HYDROLYSIS OF SAMPLE

Unless the substance is already fluid or finely divided, comminute the material in a food chopper or similar appliance and mix the sample thoroughly. Transfer a weighed sample (the amount depending upon the method of analysis selected) to a 200-ml Soxhlet flask and add water to about 175 ml. Add 3 ml of 8 *N* HCl, digest in a water bath at 80° C. for 35 minutes. Cool and add a saturated solution of normal lead acetate (about 1 ml for a 7 to 10 g sample and 3 to 6 ml for a 50-g sample). Add 2.9 ml of 8 *N* NaOH with very vigorous agitation, avoiding any local alkalinity. Make to volume, mix thoroughly, and allow to stand for several minutes. Again mix and filter. Proceed by (*b*) or (*c*).

(b) ANALYSIS BY LANE AND EYNON TITRATION AND THE MODIFIED NYNS METHOD

Weigh out an amount of the original sample which contains about 1 to 1.5 g of reducing sugar. This will vary between about 7 and 10 g. The concentration of sugar in the sample can be roughly gaged, if necessary, by refractometric examination of the juice and by assuming a total sugar purity of about 85 per cent. Hydrolyze in a 200-ml flask, defecate, make to volume 0.2 ml above the mark, and filter, as described under (*a*). Titrate the filtrate directly against 25 ml of mixed Soxhlet reagent according to Lane and Eynon's method.[7] Apply a correction to the titer (*T*) if titrations of standard solutions fail to show exact correspondence with Lane and Eynon's factors (RP426, p. 439).

Assuming that the ratio of levulose to total sugar is about 75 per cent, calculate from the total sugar titration the volume of the filtrate which contains about 75 mg of levulose. Add this volume to 50 ml of Ost's solution and add sufficient water to make 70 ml. Determine levulose as previously described (RP426, p. 425).

Calculate the ratio (*R*) of levulose to total sugar by means of Table 25 (RP426, p. 444). Refer to Table 22 (RP426, p. 439) for the proper Lane and Eynon factor. Calculate sugars in the original sample by

$$\frac{F \times 20}{T \times \text{weight sample}} = \text{per cent total sugar}$$

$$R \times \text{per cent total sugar} = \text{per cent levulose.}$$

(c) ANALYSIS BY LANE AND EYNON TITRATION AND TEMPERATURE COEFFICIENT OF POLARIZATION

Weigh out a 50-g sample, transfer to a 200-ml Soxhlet flask, hydrolyze, and defecate as described under (*a*). Make to volume 0.8 ml above the mark. Remove lead from the filtrate by addition of dry sodium oxalate or a mixture of dry oxalate and phosphate. Polarize at or near 20° C. ($=P_1$) and at about 70° C. in a water-jacketed polariscope tube, noting accurately the respective temperatures of polarization (RP426, p. 418).

Correct the high temperature polarization for the thermal expansion of the solution by

$$P_{obs.}[1 + 0.00043\ (t_2 - t_1)] = P_2$$

and calculate the per cent of levulose by

$$\frac{4(P_2 - P_1)}{0.0344(t_2 - t_1)} = \text{per cent levulose}$$

[7] J. Soc. Chem. Ind., vol. 42, p. 32, 1923. J. Assoc. Official Agr. Chem., vol. 9, p. 35, 1926. For correction to titer, see B. S. Jour. Research, vol. 8 (RP426), p. 420, 1932.

valid for a 2-dm polariscope tube. If a 4-dm tube is used divide the result by 2.

Pipette a volume of the filtrate which contains about 1 to 1.5 g of reducing sugar, make to 200 ml and titrate against 25 ml of Soxhlet's solution by Lane and Eynon's method. Calculate total sugar by

$$\frac{F\times 20\times 200}{T\times v\times 50}=\frac{F\times 80}{T\times v}=\text{per cent total sugar}$$

in which v is the volume diluted to 200 ml for titration. The factor F must be taken from the column in Table 22 (RP426, p. 439) which corresponds to the proper ratio of levulose to total sugar.

(d) PURITY OF DIFFUSION OR PRESS JUICE

The definition of purity of diffusion or press juice is to some extent arbitrary. The dry substance determination is necessarily made before the addition of the hydrolyzing agent, while the sugar analysis is made after such addition. There is therefore a change in the dry substance between the two operations. It would be possible to hydrolyze with some reagent, such as sulphuric acid, and remove it after hydrolysis with barium hydroxide. This procedure would not only be too tedious for routine analysis, but would yield the purity not of the original juice but of the defecated juice, since neutralization of the acid would be accompanied by defecation. It therefore seems advisable for practical purposes to define arbitrarily the purity as the ratio of levulose (or of total sugar) after hydrolysis to the apparent dry substance before hydrolysis. Such purity will of course be "apparent."

Dry substance determination of artichoke juices are most satisfactorily made by refractometric or densimetric estimation. A reference of such observation to Tables 18, 19, or 20 (RP426, pp. 437–438) yields "apparent" dry substance, since the tables are strictly valid only for pure levulose solutions. The dry substance can be determined by desiccation methods, but the latter are difficult because the end point of the drying is never sharply determinable. Moreover, the dry substance is still "apparent" with respect to the sugar analysis, for it consists of polysaccharides which take up water upon hydrolysis.

Having determined the apparent dry substance, weigh out a quantity of juice containing 1 to 1.5 g of total sugar and analyze as described under (*b*), or 10 to 15 g and proceed as in (*c*). Divide the percentage of levulose by percentage of dry substance to obtain the apparent purity.

(e) NOTES

The general methods described above can be applied to any plant material which contains polysaccharides similar in nature to those present in the Jerusalem artichoke, dahlia, or chicory. Only when the whole plant material is included in the sample is the allowance made for the volume of the marc.

Juices which have been hydrolyzed and defecated in preparation for the lime precipitation process can be analyzed by the methods described under (*b*) or (*c*), omitting the directions for hydrolysis. It is essential that calcium be completely removed by oxalate or oxalate-phosphate mixture, because it interferes seriously with the reducing sugar analysis.

In order to facilitate the introduction of a 50-g sample of pulped plant material into a 200-ml flask it is convenient to make use of a

brass funnel, the stem of which extends into and below the neck of the flask, and a plunger consisting of a solid brass cone with a rod attached to the smaller end.

Defecation with normal lead acetate is more complete in neutral or but slightly acid solution. The hydrochloric acid can be neutralized in the manner described if the agitation is sufficiently vigorous to avoid local alkalinity. If preferred an 8 *N* solution of potassium acetate can be substituted for the NaOH. This solution can be conveniently prepared by neutralizing about 50 g of KOH with about 47 to 50 ml of standardized glacial acetic acid and completing the volume to 100 ml.

An approximate determination of levulose in artichokes can be made by applying the Mathews formula. The filtrate from a 50-g sample is polarized directly and an aliquot volume titrated for reducing sugars. From the observed data total sugar and levulose are calculated in the manner described in RP426, p. 433. The errors in the ratio which result from the application of the Mathews formula to artichoke and dahlia juices are to be ascribed mainly to the presence of the dextrorotatory nonreducing difructose anhydrides. In Tables 1 and 2 are given the true and the Mathews ratio, the deviation of the latter averaging about 3.0 per cent of the quantity measured.

The addition of 3 ml of 8 *N* HCl is sufficient for hydrolysis if the sample contains not in excess of 19 g of dry substance. If greater weights of dry substance are present add 4 ml.

2. EXHAUSTED PULP AND PULP WATER (RAPID METHOD)

The control of the diffusion process for the extraction of juice from artichokes or similar plants requires a rapid analysis of the pulp and pulp water from the last cell of the battery as soon after its discharge as possible.

Grind the pulp sample through a food chopper and express the juice by means of a tincture press or, preferably, a hydraulic press. Pipette 100 ml into a 200-ml volumetric flask. Add 4 ml of 8 *N* HCl and immerse the flask in a boiling-water bath for four minutes. Remove from the bath and cool rapidly. Add 1 ml of saturated lead acetate and 4 ml of 8 *N* NaOH. Make to volume, filter, and titrate by Lane and Eynon's method against 25 or 10 ml of mixed Soxhlet solution according to the concentration of sugar.

$$\frac{F\times 0.2}{T} = \text{grams of reducing sugar in 100 ml}$$

Pipette 175 ml of pulp water into a 200-ml flask and add 4 ml of 8 *N* HCl. Immerse in boiling water and proceed as described in the previous paragraph.

$$\frac{F\times 0.114}{T} = \text{grams of reducing sugar in 100 ml}$$

If the concentration of sugar is too low for titration by the standard Lane and Eynon methods, titrate against one of the dilute Soxhlet reagents by the method described on page 603.

3. LEVULATE SLUDGE

Because of the instability of the reducing sugars in the alkaline medium in which calcium levulate is precipitated the levulate sludge must be sampled and neutralized without delay.

(a) TOTAL CaO

Weigh out 20 g of the thoroughly mixed sludge and wash into a porcelain casserole. Add 20 ml of Steffen's HNO_3, stir with a glass rod until completely dissolved, and boil for three to five minutes. Cool and titrate to a faint pink with Steffen's NaOH (phenolphthalein)

$$\text{Titer} \div 4 = \text{per cent CaO}$$

(b) TOTAL REDUCING SUGAR

Weigh out 15 g of the sample, wash into a porcelain casserole, and titrate to slight acidity with Steffen's HCl. Add a volume of Steffen's potassium oxalate-phosphate mixture equal to the volume of the Steffen's HCl plus a sufficient quantity to precipitate any neutral calcium which may have been introduced with the defecated juice. Wash into a 200 ml volumetric flask, make to volume, and add by means of a graduated pipette an excess of water equal to the volume of the precipitate. (See p. 604.) Filter and titrate directly against 25 ml of mixed Soxhlet solution by Lane and Eynon's method for total reducing sugars. Calculate by

$$\frac{4 \times F}{3 \times T} = \text{per cent reducing sugar}$$

in which F is Lane-Eynon's factor and T the corrected titer.

(c) LEVULOSE

In most instances the ratio of levulose to total reducing sugar will have been determined previous to the precipitation process. If so, the known ratio can be applied to the percentage of total reducing sugar to compute the percentage of levulose. The latter can be determined by analysis of the above filtrate by taking a volume containing about 75 mg of levulose and proceeding by the modified Nyns method as described in RP426, page 425. Calculate the ratio, R, as described in RP426, page 444.

$$R \times \text{per cent total sugar} = \text{per cent levulose}$$

4. LEVULATE CAKE

(a) TOTAL CaO

Weigh out 10 g of the sample and wash into a porcelain casserole. Add an excess (usually 25 ml) of Steffen's HNO_3. Stir with a glass rod until dissolved, place over a flame, and allow it to boil from three to five minutes. Add a few drops of phenolphthalein and titrate to a faint pink with Steffen's NaOH.

$$\text{Titer} \div 2 = \text{per cent CaO}$$

(b) TOTAL SUGAR AND LEVULOSE

Weigh out 20 g of the sample, wash into a porcelain casserole, and titrate to slight acidity with Steffen's HCl (phenolphthalein). Wash into a 200 ml volumetric flask. Add a volume of Steffen's oxalate-phosphate mixture slightly in excess of the determined volume of Steffen's HNO_3 which was required for the CaO determination. Make to volume and add an excess of water equal to the volume of the precipitate, that is, 0.065 × milliliters of Steffen's reagents used.

Polarize the filtrate, preferably in a 400 mm tube, at or near 20° C., recording the temperature of observation. The negative polarization of levulose is enhanced in the presence of KCl, 1 g in 100 ml increasing it in the negative sense by 0.59 per cent. Since there is formed 0.1332 g of KCl for each milliliter of Steffen's reagent added, diminish the negative polarization by 0.078 per cent of its value for each milliliter of Steffen's reagent used.

Pipette 50 ml of the filtrate into a 200 ml flask, make to volume, and titrate against 25 ml of Soxhlet's solution.

From the corrected polarization and the corrected titer calculate the Mathews ratio in the manner described on p. 440, RP426, remembering that the polarization, P, in the formula refers to the rotation in a 2 dm column. Calculate by

$$\frac{F \times 4}{T} = \text{per cent total sugar},$$

and

$$R \times \text{per cent total sugar} = \text{per cent levulose}$$

5. WASTE WATER

(a) CaO

Weigh out 100 g of the sample, wash into a porcelain casserole, and titrate with Steffen's HCl (phenolphthalein). Save the solution for (*b*) and (*c*).

$$\text{Titer} \div 20 = \text{per cent CaO}$$

(b) TOTAL SUGAR

Wash the titrated solution into a 200 ml volumetric flask and add a volume of Steffen's oxalate-phosphate mixture equal to the titer for CaO. If the solution is derived from a juice which has been hydrolyzed with H_2SO_4 and defecated with lime, add an additional 15 ml of the oxalate-phosphate mixture. The calcium must be completely removed. Make to volume and add an excess of water equal to the volume of the precipitate; that is, 0.065 × milliliters of Steffen's reagent. From the filtrate pipette a volume containing about 1 g of total sugar into a 200 ml volumetric flask, make to volume, and titrate against 25 ml of mixed Soxhlet reagent.

(c) LEVULOSE

Assuming a ratio of levulose to total sugar of 35 per cent, compute the volume of the original filtrate which contains about 75 mg of "apparent" levulose, add this volume to 50 ml of Ost's reagent, make to 70 ml, and proceed as directed on page 425, RP426. Cal-

culate the ratio of levulose to total sugar in the usual way by referring to Table 22 (RP426, p. 444) and find the total sugar and levulose by the following formulas:

$$\frac{40 \times F}{T \times v} = \text{per cent total sugar}$$

where F is Lane and Eynon's factor, T is the Lane and Eynon titer, and v is the volume of solution which was diluted to 200 ml for the titration:

$$\text{Per cent total sugar} \times R = \text{per cent levulose}$$

Some uncertainty is introduced by assuming a value for the neutral calcium which is precipitated. The variations from the value given above will, in general, be within the analytical accuracy. If desired, the calcium can be precipitated by dry sodium oxalate and the uncertainty avoided.

6. EVAPORATOR LIQUORS

The levulose solutions which are prepared by carbonation of the levulate cake are of relatively high purity. After filtration from the calcium carbonate they are freed from calcium bicarbonate by evaporation or other means and filtered. At this point an analysis is of significance in determining the completeness of the separation of levulose from its impurities.

It has already been shown that for artichoke juices the Mathews ratio differs but slightly from the true ratio, a fact which indicates that the optically active substances in the juice are mainly levulose and dextrose. It follows, then, that in the purified liquors from which most of the impurities have been removed the Mathews ratio will approach the true ratio very closely. Inasmuch as the analytical operations contributing to the determination of the Mathews ratio are far more precise and reproducible than those depending upon Nyns's method, it is to be recommended that the levulose purity of high purity liquors be determined on the basis of the Mathews ratio solely.

(a) DRY SUBSTANCE

Determine dry substance by measurement of density, referring the observation to Tables 18 or 19 (RP426, p. 437), or by refractometer reading, referring to Table 20 (RP426). If the sirup has too high a concentration for the polarization which is to follow, it must be diluted to below 17.2 per cent for a 20° C. polarization, or below 17.9 per cent for 25° polarization. In this case the dry substance measurement must be repeated for the diluted solution, or a weighed amount of the concentrated solution must be diluted with a weighed amount of water.

(b) DIRECT POLARIZATION AND APPARENT PURITY

Polarize the diluted solution directly, recording the temperature of observation accurately. From this observation and the percentage of dry substance of the solution the "apparent" purity can be calculated by assuming that all optically active material is levulose. Correct the direct polarization to either 20° or 25° C. by assuming an expansion coefficient of 0.00043 and a polarization temperature

coefficient of 0.0344° S. for each gram of levulose per degree change of temperature. Correct for concentration by Table 21 (RP426, p. 439). Multiply the normal weight (18.407 g at 20° C. or 19.003 g at 25° C.) by the direct polarization and divide by the number of grams of dry substance in 100 ml. (See below.)

(c) TOTAL SUGAR

Compute from the polarization or dry substance analysis the volume of solution containing about 1 g of total sugar. Transfer this volume to a 200-ml volumetric flask, make to volume, and titrate against 25 ml of mixed Soxhlet reagent.

(d) TRUE PURITY

From the direct polarization and reducing sugar titration compute the product $P \times T/D$ and determine the ratio of levulose to total sugar by reference to Table 24 (RP426, p. 442; see also example on p. 440). The true purity of the sample is

$$\frac{F \times R \times D}{T \times S \times 10} = \text{per cent purity}$$

in which F is Lane and Eynon's factor, R the Mathews ratio, T the corrected titer, D the number of volumes to which the solution polarized was diluted for titration, and S the grams of dry substance in 100 ml of the solution polarized. The latter is determined by multiplying the percentage of dry substance by the density as given in Table 18 (RP426, p. 437). This product is the weight of dry substance in vacuo and for precise work should be diminished by 0.11 per cent of its value to give its weight in air with brass weights.

V. HONEY AND VARIOUS FRUITS

The methods of selective levulose analysis are applicable to any product containing levulose. In order to illustrate further possible applications, we have analyzed samples of honey and such fruits as were immediately available.

The samples of honey were supplied by the Bee Culture Laboratory, of the United States Department of Agriculture. Dry substance determinations were made by C. F. Snyder, of this bureau, by refractometer readings referred to Table 20 (RP426, p. 438). The samples were prepared for analysis by weighing out 20 g and washing into 200-ml volumetric flasks. The solutions were clarified satisfactorily by addition of alumina cream. Sucrose was estimated by determining polarizations before and after inversion with invertase. Both the original and inverted solutions were subjected to a complete sugar analysis by the general procedure outlined on pages 604–606. Before calculating the Mathews ratio, the rotation of the sucrose was deducted from the direct polarization.

The analytical data are assembled in Table 5. This group of samples showed a ratio of levulose to total sugar not greatly in excess of 50 per cent; the ratio is therefore not appreciably altered by the inversion of the sucrose. The deviation of the Mathews ratio from the true ratio has been solved by formula (3) under the arbitrary assumption that the deviation is due to dextrins. If a specific rotation of

+150° C.[8] is assigned to these substances, the constant c in formula (2) acquires a value of 11.5. It is apparent from columns 8 and 13 that these substances occur in all the samples analyzed and that normal nectar honeys contain a mean of about 4.6 per cent. Obviously, if honey were adulterated with any considerable quantity of invert sugar, the deviation of the Mathews ratio from the true ratio will diminish. The suggestion is made that this method of grouping these substances under the designation "apparent dextrins" may be useful in the critical examination of honey. In the honey dew and the melezitose honey the quantity of apparent dextrins becomes very large. The melezitose honey shows no significant change in ratio or in the apparent dextrins before and after inversion, indicating that melezitose is unaffected by invertase. In confirmation of this fact, a sample of pure melezitose showed no change in polarization after treatment with invertase. The total carbohydrates in the melezitose honey fall far short of the total dry substance. This arises from the fact that we ascribed a specific rotation of +150 to the undertermined carbohydrates. If we make the assumption that the total carbohydrate purity is 98.2 per cent (the mean of the remaining honeys) and assign a specific rotation of +150 to the dextrins and +87.8 to melezitose, we can solve simultaneously for the two latter substances. Such a solution yields values of 3.9 per cent dextrins and 20.2 per cent melezitose.

The samples of fruit were obtained by purchase from commercial sources. No attempt was made to secure representative samples, since the purposes of the present article were merely to illustrate the applicability of the methods of analysis. Although some of the fruits were "out of season" at the time of the analysis (March), they were in every case firm and sound.

The analyses refer only to the press juice which was obtained by extraction of the comminuted sample in a small tincture press. Considerable difficulty was encountered in the filtration of the solution after defecation with normal lead acetate, but this was overcome in some cases by sedimentation in a centrifugal machine. The solutions from the deeply colored fruits in some cases remained discolored after defecation, but were completed bleached by one or two drops of a 0.5 *N* sulphur dioxide solution.

One hundred grams of the sample of press juice was transferred to a 200 ml flask, defecated with normal lead acetate, and filtered or sedimented. Lead was removed by adding a mixture of dry sodium phosphate and sodium oxalate. Sucrose was determined by the invertase method, and total sugars and levulose by the methods previously described. The ratio of levulose to total sugar as determined by the Mathews formula was derived from the titer and from the direct polarization corrected for the rotation of sucrose.

The analytical data are shown in Table 6. It is noteworthy that all of the fruits examined, except the cranberries, showed an excess of levulose, slight in many cases, but rising to great predominance in apples and pears. The deviation of the Mathews ratio from the true ratio as shown in column 8 is small in all cases except the peach and the cranberry in which it assumes large negative values. This indicates the presence of a levorotatory substance.

[8] Browne's Handbook of Sugar Analysis, p. 523. John Wiley & Sons, New York, 1912.

TABLE 5.—*Analyses of honeys*

Principal floral source of honey	Original honey						
	Dry substance	Sucrose	Reducing sugars	Levulose	Ratio: Levulose / reducing sugar	Mathews ratio: Levulose / reducing sugar	Apparent dextrins
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Sumac	82.54	3.26	72.13	37.53	51.9	43.2	5.81
White clover	82.42	1.69	76.09	39.26	51.6	46.9	3.32
Buckwheat	81.08	.44	75.53	38.97	51.6	46.3	3.71
Blend No. 1	82.42	1.61	78.69	42.02	53.4	50.3	2.26
Alfalfa	85.68	4.73	76.05	39.63	52.1	44.8	5.15
Sourwood	82.46	1.41	69.17	38.94	56.3	44.8	7.99
Fireweed	84.48	4.54	74.76	40.97	54.8	47.4	5.12
Wallberry	83.24	.83	73.20	41.14	56.2	48.5	5.21
Goldenrod	82.16	.68	77.08	39.93	51.8	47.0	3.43
Blend No. 2	84.84	1.65	77.81	39.92	51.3	45.8	3.97
Honey dew (incense cedar)	86.44	2.90	61.05	28.95	47.4	11.4	20.43
Melezitose honey	83.50	.30	57.61	32.57	56.5	27.0	15.70

Principal floral source of honey	Honey after invertase inversion				
	Reducing sugars	Levulose	Ratio: Levulose / reducing sugar	Mathews ratio: Levulose / reducing sugar	Apparent dextrins
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Sumac	75.50	38.96	51.6	43.4	5.75
White clover	77.70	40.09	51.6	46.9	3.39
Buckwheat	75.67	39.12	51.7	46.3	3.80
Blend No. 1	79.11	41.37	52.3	50.4	1.40
Alfalfa	80.45	41.11	51.1	45.1	4.49
Sourwood	70.27	39.56	56.3	43.9	8.07
Fireweed	79.01	43.22	54.7	47.5	5.28
Wallberry	74.13	41.74	56.3	48.3	5.49
Goldenrod	77.32	40.52	52.4	47.1	3.80
Blend No. 2	79.23	40.80	51.5	45.8	4.20
Honey dew (incense cedar)	62.78	30.62	48.8	12.5	21.17
Melezitose honey	57.96	33.26	57.4	27.0	16.27

TABLE 6.—*Analyses of fruits*

Fruit	Dry substance by refractometer	Sucrose	Reducing sugars	Levulose	Ratio: Levulose / reducing sugar	Mathews ratio: Levulose / reducing sugar	ΔR	Total sugar purity
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Peach, "Old Gold"	16.50	8.62	3.17	1.82	57.4	63.8	−6.4	71.5
Apple, "Delicious"	13.14	1.80	9.63	6.58	68.3	69.8	−1.5	87.0
Pear, "D'Anjou"	17.06	1.24	9.99	8.88	88.9	86.7	2.2	65.8
Lemon	8.33	.40	2.03	1.07	52.9	51.8	1.1	29.2
Orange	12.07	4.50	5.07	2.65	52.2	51.7	.5	79.3
Grapefruit	13.84	4.03	6.05	3.17	52.5	51.3	1.2	72.8
Grapes, "Almeria"	18.05	.19	16.28	8.32	51.1	48.6	2.5	91.2
Strawberry	7.63	.82	4.09	2.20	53.8	51.2	2.6	66.4
Cranberry	9.93	.24	5.18	.82	15.8	30.5	−14.7	54.6
Tomato	4.67	0	2.79	1.58	57.7	56.3	1.4	59.7

WASHINGTON, August 13, 1932.

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DETERMINATION OF ALUMINA AND SILICA IN STEEL BY THE HYDROCHLORIC ACID RESIDUE METHOD

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ABSTRACT

The hydrochloric acid residue method, as used at the Bureau of Standards for the determination of alumina and silica in steels, is described. Analyses of six steels indicate that this method yields results for both alumina and silica which compare favorably with those obtained by the bromine and nitric acid residue methods. Of the three methods, the hydrochloric acid method is preferred on the grounds of speed and simplicity of operation.

Data are presented to show that the presence of aluminum nitride in a steel does not cause appreciable errors in the determination of alumina by the hydrochloric acid residue method.

The recovery of manganese oxide and silica from manganese silicates, by means of the hydrochloric-acid-residue method, is discussed. Data are presented to show that satisfactory recovery of silica is obtained only from silicates rich in silica and that satisfactory recovery of manganese oxide is not obtained by this method.

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I. INTRODUCTION

The use of dilute hydrochloric acid to effect the separation of metallic and nonmetallic constituents of steel was first applied to the determination of alumina in steel by Kichline [1] who reported that not more than 1 or 2 per cent of the alumina (Al_2O_3) present is soluble in dilute hydrochloric acid. He recommended decomposition of the sample in diluted acid (2+3) with subsequent determination of alumina in the residue by the phosphate method.

Oberhoffer and Ammann [2] confirmed Kichline's conclusions regarding the insolubility of alumina in diluted hydrochloric acid and presented comparative analyses made by the bromine method and by the hydrochloric-acid method. The results obtained by the two methods are in satisfactory agreement, although the values obtained by the bromine method usually are slightly higher than those obtained by the hydrochloric-acid method.

[1] F. O. Kichline, Note on the Determination of Aluminum Oxide and Total Aluminum in Steel, J. Ind. Eng. Chem., vol. 7, pp. 806-807, 1915.

[2] P. Oberhoffer and E. Ammann, Ein Beitrag zur Bestimmung Oxydischer Einschlüsse in Roheisen und Stahl, Stahl u. Eisen, vol. 47, pp. 1536-1540, 1927.

At the Bureau of Standards it was found that the hydrochloric-acid-residue method could be modified to permit the determination of silica (SiO_2) as well as alumina. The principal modification consists in the use of the 3 per cent sodium carbonate washing solution which Oberhoffer and Ammann employed to separate silica and hydrated silicic acid in the residues obtained in their modified bromine method. The silica in the residue originates in silica and silicate inclusions in the steel. The hydrated silicic acid originates in the decomposition of metallic silicides, and must be separated from the silica before an accurate determination of the latter can be made. The residue which remains after treatment with the acid and alkali solutions may be analyzed by several methods, but it is believed that a complete description of the procedure in use at the Bureau of Standards will be of interest. This procedure is described in the succeeding section.

II. METHODS OF ANALYSIS

1. DETERMINATION OF SILICA AND ALUMINA

Dissolve 50 g of steel chips in 500 ml of diluted hydrochloric acid (1+2) on the steam bath. After solution of the iron is complete, filter, with moderate suction, through a tight paper containing a little ashless paper pulp. Wash the residue[3] on the filter several times with cold water or with diluted hydrochloric acid (1+20) and then with hot water until the filter paper is free from iron salts. Wash the residue further with 500 ml of hot (80° to 90° C.) 3 per cent sodium carbonate solution, followed by successive washings with hot water, 50 ml of diluted hydrochloric acid (1+20) and finally with hot water. The diluted hydrochloric acid removes hydrated iron salts and any sodium silicate which may have formed in dissolving the hydrated silicic acid.

Transfer the paper and residue to a platinum crucible,[4] and heat gently so as to char the paper without allowing it to flame. Finally increase the temperature and ignite, under good oxidizing conditions, but do not let the temperature rise above very dull redness (about 600° C). Fuse with a small amount of sodium carbonate (2 g will usually suffice). Cool, and dissolve in 50 ml of diluted hydrochloric acid (1+10). If a residue remains, filter and wash. Reserve the filtrate designating it (*A*). Ignite paper and residue in a platinum crucible, fuse with 3 g of potassium pyrosulphate, dissolve the cooled melt in a small volume of dilute hydrochloric acid and add to the reserved filtrate (*A*).

Silica.—Evaporate the solution (*A*) to dryness and bake for one hour at 105° C. Cool, drench with 10 ml of hydrochloric acid and digest a few minutes. Add 75 ml of warm water to dissolve salts, filter, and wash several times with cold diluted hydrochloric acid (1+10) and then with warm water. Reserve the filtrate, designating it (*B*). Ignite the paper and contents in a platinum crucible, slowly at first, and finally at a temperature of 1,200° C. for about 25 minutes. Cool, weigh, volatilize silica by the usual hydrofluoric-sulphuric acid treatment and reweigh. Any residue remaining in the crucible is dissolved in hydrochloric acid, or fused with bisulphate and added to the reserved filtrate (*B*).

[3] The residue may contain carbides of alloying elements, such as chromium and vanadium.

[4] With some steels, such as those which contain appreciable amounts of copper, it is advisable to ignite (not over 600° C.) in porcelain and subsequently transfer the residue to platinum for the fusion treatment.

Alumina.—Adjust the volume of the filtrate (*B*) to about 100 ml, add 2 ml of strong sulphurous acid,[5] and boil vigorously to expel the excess sulphur dioxide. Add 4 ml of concentrated nitric acid to the hot solution and boil to oxidize ferrous iron. Add sodium hydroxide solution until the acid solution is nearly neutral. Pour the nearly neutral solution slowly and with constant stirring into 80 ml of an 8 per cent solution of sodium hydroxide. Heat to boiling, remove from the source of heat, and allow to stand for at least two hours to permit the precipitate to settle. Filter through a double filter of a strong tight paper (No. 42 Whatman), and wash with a 1 per cent solution of sodium hydroxide.

Acidify the filtrate with hydrochloric acid and concentrate to a volume of about 250 ml. Add 5 ml of concentrated hydrochloric acid and 0.5 g of diammonium phosphate. The addition of a little macerated filter paper will prevent gelatinous aluminum phosphate, formed subsequently, from coagulating in lumps which are difficult to wash free from sodium and ammonium salts. Add two drops of methyl red indicator, make the solution just ammoniacal and restore the pink color with several drops of diluted hydrochloric acid (1+20). Heat the solution to boiling, add 20 ml of a 20 per cent solution of ammonium acetate and boil for five minutes. Let stand for 1 to 2 hours, filter through a tight 9 cm paper (No. 42 Whatman) and wash with hot 5 per cent solution of ammonium nitrate until 10 ml of the washings no longer yield a test for chlorides with acidified silver nitrate. Ignite the residue and paper in platinum under good oxidizing conditions until carbon is gone; cover, and heat at about 1,000° C, to constant weight. The observed weight of aluminum phosphate multiplied by the factor 0.418 is recorded as the weight of Al_2O_3 present in the original residue. Blank determinations are made on all reagents used, and the proper corrections are applied to the results of each analysis.

2. DETERMINATION OF MANGANOUS OXIDE

Any manganese present in the original residue will be found with the iron and chromium precipitated by the sodium hydroxide treatment. If manganese is to be determined, dissolve this precipitate of iron, chromium, and manganese with 50 ml of warm diluted nitric acid (1+3) containing a few milliliters of sulphurous acid. Boil the solution to expel the oxides of nitrogen, allow to cool, and determine manganese by the bismuthate method. If the amount of manganese is very small it is better to use the periodate colorimetric method.[6]

III. EXPERIMENTAL RESULTS

1. BEHAVIOR OF ALUMINUM NITRIDE IN THE DETERMINATION OF ALUMINA

The question arose whether aluminum nitride, if present in the steel, would be found in the acid-insoluble residue and carried through the determination and reported as alumina. To investigate this possi-

[5] The sulphurous acid, made by passing sulphur dioxide into distilled water to saturation, is added to reduce any oxidized chromium in order that all of the chromium present may be removed subsequently with the iron. The reduction of chromium by means of hydrogen peroxide was tried, but difficulty was encountered in the subsequent removal of iron from the solution, perhaps due to the formation of small amounts of soluble sodium ferrate.

[6] H. H. Willard and L. H. Greathouse, The Colorimetric Determination of Manganese by Oxidation with Periodate, J. Am. Chem. Soc., vol. 39, pp. 2366–2376, 1917.

bility, a quantity of aluminum nitride, containing 10.1 per cent nitrogen, was obtained through the courtesy of the Fixed Nitrogen Research Laboratory, of the U. S. Department of Agriculture.

Two portions of approximately 50 mg each were treated in separate beakers with 50 ml of diluted hydrochloric acid (1 + 2). After standing on the steam bath overnight, the solutions were filtered and the residues on the filter papers were washed as in the regular procedure for the separation of acid-insoluble residues. The residues were ignited at a dull red heat to destroy carbonaceous matter, cooled, and transferred together with 50 ml of hydrochloric acid (1 + 1) to distilling flasks for the determination of nitrogen by the Allen method. Nitrogen is the only constituent of aluminum nitride which was determined, as it was assumed that any attack on the nitrides, by either acid or alkaline solutions, which resulted in solution of the nitrogen, would result in the simultaneous solution of an equivalent amount of aluminum. In other words, if nitrogen dissolves from aluminum nitride, in either acid or alkaline solutions, aluminum likewise will dissolve.

The data obtained from these two samples showed that the insoluble residues contained less than 4 per cent of the nitrogen present in the original samples. This indicates that at least 96 per cent of synthetic aluminum nitride is soluble in the hydrochloric acid (1 + 2) or in the wash solutions.

In addition to the above, tests were also made on nitrided samples of two commercial steels, one of the aluminum-molybdenum type and the other of the aluminum-molybdenum-chromium type, obtained through the courtesy of Dr. V. O. Homerberg. The composition of these steels prior to nitriding is recorded in Table 1. Specimens for residue analysis consisted of thin nitrided disks, approximately one-sixteenth inch thick and five-eighths inch in diameter, chosen on the assumption that with such thin sections practically all of a specimen would be affected by the nitriding treatment.

Samples of each nitrided steel were subjected to the different operations of a residue analysis, as follows: The samples designated *A* in Table 1 were decomposed in hydrochloric acid (1 + 2), filtered, and the acid-insoluble residues were washed with the customary solutions. Nitrogen was determined separately in the original filtrates, in the wash waters, and in the unignited residues. The samples designated *B* in Table 1 were decomposed in hydrochloric acid (1 + 2), filtered without washing, and nitrogen was determined in the filtrates and residues.

The results recorded in Table 1 show that the nitrides present in these two nitrided steels were almost completely decomposed and dissolved by the first solution treatment with hydrochloric acid (1 + 2) in the usual procedure of residue analysis. The amounts of nitrogen recovered either from the wash waters or from the insoluble residues were of approximately the order of magnitude of the blank correction. However, small but positive traces of nitrogen usually were indicated, as recorded in Table 1. These data show that the amounts of nitrides which survived the solution in acid but dissolved in the wash waters were negligible. The amounts of nitrides retained in the insoluble residues in all cases were an insignificant proportion of the nitrides present in the original sample.

TABLE 1.—*Behavior of nitrides in residue analysis of two nitrided steels*

Sample No.	Weight of sample	Nitrogen recovered		
		Filtrate	Wash waters	Residue
	g	*g*	*g*	*g*
225A	5.858	0.1000	0.00008	0.0002
225A	4.613	.0720	Nil.	.00014
225B	6.174	.1115		.00007
225B	5.247	.0870		.0002

COMPOSITION OF STEELS BEFORE NITRIDING

Steel No.	C	Mn	P	S	Si	Al	Mo	Cr
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
225	0.19	0.38	0.014	0.012	0.16	1.88	0.83	
225	.35	.48	.018	.020	.15	.90	.20	0.99

It is concluded, therefore, that the small amounts of aluminum nitride ordinarily present in nonnitrided steels (or in the interior portions of nitrided ones) do not interfere with the determination of alumina by the hydrochloric acid residue procedure. However, in the case of nitrided steels if we assume that all residual nitrogen was present as aluminum nitride and calculate to the equivalent Al_2O_3 we find an appreciable error would occur in the determination of Al_2O_3, particularly if the latter were present in very small amounts.

2. COMPARISON OF RESULTS OBTAINED FROM DIFFERENT RESIDUE METHODS

The data in Table 2 are the results obtained for alumina and silica in comparative analyses of six steels by the nitric acid,[7] the bromine, and the hydrochloric acid residue methods.

The results obtained for alumina are in satisfactory agreement for all three methods. It is believed, however, that the hydrochloric acid residue method is preferable, as it is more rapid and more convenient to operate than either the nitric acid or the bromine methods.

In the determination of silica, the results from the modified hydrochloric acid method and the bromine method are in satisfactory agreement, but some of the results from the nitric acid method are lower than results from either of the other two. The lower results from the nitric acid method probably can be explained on the basis of Oberhoffer and Ammann's statement that the sodium hydroxide wash used in the nitric acid method not only dissolves hydrated silicic acid but also attacks dehydrated silica.

[7] J. H. S. Dickenson, A Note on the Distribution of Silicates in Steel Ingots, J. Iron & Steel Inst., vol. 113 (No. I), pp. 177–196, 1926.

TABLE 2.—*Comparison of results obtained by different residue methods for alumina and silica*

Type of steel	Sample No.	Mold additions for 3 tons of steel	Al_2O_3			SiO_2		
			Hydrochloric-acid method	Bromine method [1]	Nitric-acid method [1]	Hydrochloric-acid method (modified)	Bromine method [1]	Nitric-acid method [1]
			Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Killed steel (0.14 C, 0.44 Mn, 0.15 Si)	113	4 pounds Al	0.026	0.023	0.022	0.001	0.002	<0.00
	119	25 pounds Fe–V	.003	.002	.003	.004	.006	.00
	122	None	.002	.002	.001	.008	.006	.00
Effervescing steel (0.14 C, 0.42 Mn, 0.003 Si)	125	4 pounds Al	.014	.016	.017	<.001	.001	.00
	131	25 pounds Fe–V	.002	.002	<.001	.008	.009	.01
	134	None	.001	--------	<.001	<.001	--------	<.00

[1] Analyses by the bromine method were made by R. J. Kranauer, formerly of the Bureau of Standards. Analyses by the nitric-acid method were made by H. A. Bright.

3. RECOVERY OF SILICA AND MANGANOUS OXIDE FROM SYNTHETIC MANGANESE SILICATES

In analyses of acid-insoluble residues by the hydrochloric acid method, it was frequently observed that the sodium carbonate fusions were colored green, indicating the presence of manganese. It is probable that manganous oxide, if present in the steel, would be soluble in hydrochloric acid (1+2), but it is possible that certain manganese silicates, if present, would be insoluble and, therefore, would appear in the residue. In order to investigate this possibility, synthetic manganese silicates containing different proportions of manganous oxide and silica were prepared, and the amounts of manganous oxide and silica recovered by the modified hydrochloric acid residue method were determined.

Manganous oxide was prepared in the laboratory from manganese carbonate by two methods. In one method the carbonate was oxidized to MnO_2 by treatment with nitric acid. The MnO_2 was reduced to MnO by heating in a nickel boat in a stream of hydrogen at 900° C. for about four hours. In the other method manganese carbonate was calcined in air at about 1,200° C. in a graphite crucible in the induction furnace, and was then further heated at 1,500° C. in graphite in a vacuum.

Three manganese silicates, intended to contain 25, 50, and 75 per cent MnO, respectively, were prepared by mixing precipitated manganese carbonate and pulverized quartz in the proper proportions and heating each mixture in a graphite crucible to about 1,500° C. After cooling in the furnace the melt was cleaned on an emery wheel and then crushed and ground. In the course of the investigation it appeared that manganese silicates of additional compositions were needed. Such silicates, containing approximately 30 and 60 per cent MnO, respectively, were supplied by Dr. C. H. Herty, jr., of the Bureau of Mines.

The manganese silicates, manganous oxide, and quartz used in the analyses were ground to pass through a No. 120 sieve. The two silicates received from Doctor Herty passed through a No. 200 sieve. Each sample for residue analysis consisted of about 10 mg of one of the finely ground materials mixed with 50 g of drillings of vacuum-

fused electrolytic iron. Fifty-gram portions of drillings, without additions, frequently were run as blank determinations.

The results obtained for the recovery of manganous oxide and silica from these synthetic manganese silicates, by the modified hydrochloric acid residue method, are presented in Table 3 and are shown graph-

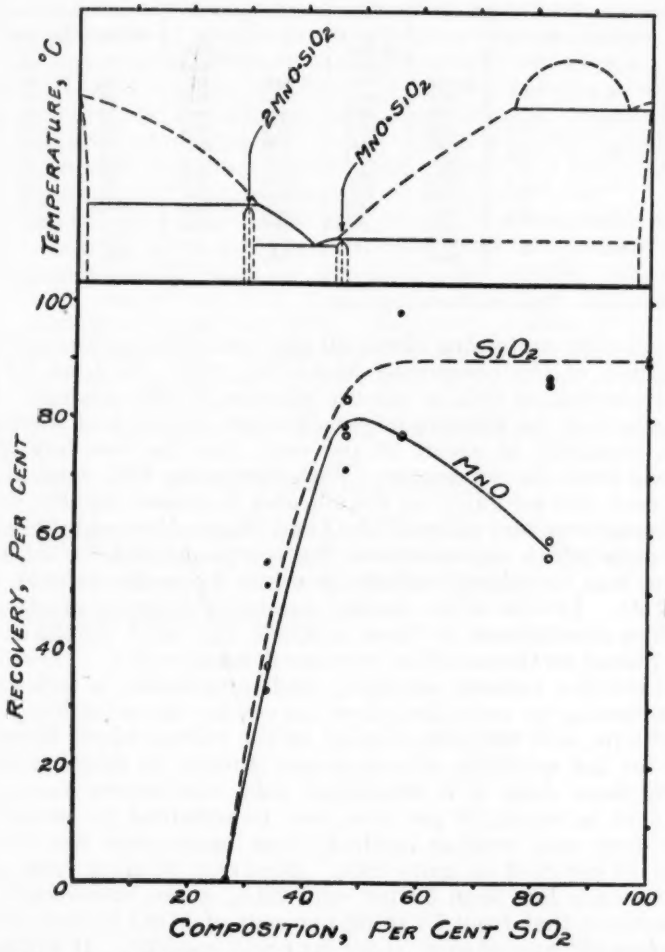

FIGURE 1.—*Recovery of MnO and SiO_2 from synthetic manganese silicates by the hydrochloric acid residue method*

ically in Figure 1. The equilibrium diagram for the system MnO–SiO_2[8 9] is included in Figure 1 for convenience in interpreting the results.

[8] C. Benedicks and H. Löfquist, Nonmetallic Inclusions in Iron and Steel, Chapman & Hall, London, p. 98, 1930.

[9] C. H. Herty, jr., and G. R. Fitterer, New Manganese Silicon Alloys for the Deoxidation of Steel, U. S. Bureau of Mines Report of Investigations, R. I. 3081, 1931.

TABLE 3.—*Recovery of MnO and SiO_2 from synthetic manganese silicates*

Composition of sample		Weight taken		Weight found		Recovery	
MnO	SiO_2	MnO	SiO_2	MnO	SiO_2	MnO	SiO_2
Per cent	*Per cent*	*g*	*g*	*g*	*g*	*Per cent*	*Per cent*
0.	100		0.0104		0.0093		89
			.0100		.0090		90
16.4	82.7	0.0016	.0083	0.0009	.0071	56	86
		.0017	.0084	.0010	.0073	59	87
[1] 30.2	[1] 56.3	.0035	.0065	.0027	.0064	77	98
		.0035	.0065	.0027	.0064	77	98
50.7	47.0	.0062	.0058	.0048	.0041	77	71
		.0053	.0049	.0044	.0038	83	78
[1] 58.2	[1] 33.7	.0062	.0036	.0023	.0020	37	55
		.0060	.0035	.0020	.0018	33	51
70.0	26.5	.0070	.0027	.0000	.0000	Nil.	Nil.
		.0073	.0028	.0000	.0000	Nil.	Nil.
100.0	0.	.0109		.0000		Nil.	
		.0101		.0000		Nil.	

[1] 200-mesh samples. Other samples were 120 mesh.

The silicates containing about 50 per cent SiO_2, approximately the composition of the compound $MnO.SiO_2$, were the least soluble in dilute hydrochloric acid of all the silicates in this system. As the SiO_2 content of the silicates increased above 50 per cent the recovery of SiO_2 remained at about 90 per cent, but the recovery of MnO decreased from the maximum. With decreasing SiO_2 content, below 50 per cent, the solubility of the silicates increased rapidly, resulting in decreased recovery of both MnO and SiO_2 in the insoluble residues. The sample which approximated the compound $2MnO.SiO_2$ in composition, was completely soluble in dilute hydrochloric acid, as was pure MnO. In view of the limited number of determinations and the difficulties encountered in these analyses, too much emphasis should not be placed on the results of any one determination. However, the general relation between solubility and composition is indicated and it is interesting to note that these curves for the solubility in dilute hydrochloric acid are quite similar to the curves which Herty [10] obtained for the solubility of manganese silicates in dilute nitric acid.

From these data it is concluded that satisfactory recoveries of silica, that is, about 90 per cent, can be obtained by means of the hydrochloric acid residue method, from manganese silicates which contain 50 per cent or more SiO_2. Recovery of silica from silicates which contain less than 50 per cent SiO_2, is not satisfactory. The data indicate that from 70 to 80 per cent of MnO is recovered from manganese silicates of over 50 per cent SiO_2 content. It will be noted that the revovery of MnO in silicates of less than 50 per cent SiO_2 is quite low. Obviously, the HCl method is not applicable to the determination of MnO occurring as such (MnO inclusions) and yields only fair recoveries of MnO in manganese silicates of high silica content.

[10] C. H. Herty, jr., G. R. Fitterer, and J. F. Eckel, The Physical Chemistry of Steel Making: A Study of the Dickenson Method for the Determination of Nonmetallic Inclusions in Steel, U. S. Bureau of Mines Mining, and Metallurgical Investigations Bull. No. 37, 1928.

IV. SUMMARY

1. The conclusions of previous investigators that the hydrochloric acid residue method yields results for alumina that are comparable with those obtained by the nitric acid and bromine methods, and that the hydrochloric acid method is preferable to the other two on the grounds of speed and simplicity in operation, have been confirmed.

2. The presence of aluminum nitride in a sample ordinarily does not cause appreciable errors in the determination of alumina by the hydrochloric acid residue method. If relatively large amounts of nitrides are present; for example, in a nitrided steel, accompanied by only a small amount of aluminum oxide, a small error due to incomplete decomposition of aluminum nitride might result in a serious error in the determination of a small amount of aluminum oxide.

3. The modified hydrochloric acid residue method yields as satisfactory results for silica as do the nitric acid and bromine methods.

4. If manganese silicates are present in the sample, recoveries of about 90 per cent of the silica may be obtained from silicates which contain more than 50 per cent SiO_2. Recovery of silica from silicates which contain less than 50 per cent SiO_2 is not satisfactory. The hydrochloric acid method recovers about 70 to 80 per cent of MnO from manganese silicates having 50 per cent or more SiO_2 content. The method is not suitable for MnO in silicates of less than 50 per cent SiO_2.

V. ACKNOWLEDGMENT

Acknowledgment is made to H. A. Bright, who is responsible for the section on methods of analysis, and who has contributed helpful advice on other phases of the work reported herein.

WASHINGTON, August 17, 1932.

AN ANALYSIS OF LANTHANUM SPECTRA (LA I, LA II, LA III)

By Henry Norris Russell [1] and William F. Meggers

ABSTRACT

All the available data (wave-length measurements and intensity estimates, temperature classes, Zeeman effects) on lanthanum lines have been correlated and interpreted in an analysis of the successive optical spectra. The total number of lines classified is 540 in the La I spectrum, 728 in the La II spectrum, and 10 in the La III spectrum.

Series-forming terms have been identified in each spectrum and from these the ionization potentials of 5.59 volts for neutral La atoms, 11.38 volts for La^+ atoms and 19.1 volts for La^{++} atoms have been deduced.

Lanthanum is a chemical analogue of scandium and yttrium, but, although the corresponding spectra are strikingly similar, some interesting differences are noted. A doublet-D term (from a d electron) represents the lowest energy (normal state) in the third spectrum of each element and another ^2D (from the sd configuration) describes the normal state of the neutral atoms in each case. The homologous atoms Sc^+, Y^+, La^+ choose different normal states; (sd) ^3D, (s^2) ^1S, (d^2) ^3F, respectively. In addition, the first two spectra of La exhibit a large number of (odd) middle-set terms ascribed to the binding of an f electron. The La II spectrum is the most completely developed example of a two-electron spectrum which has yet been investigated. All the configuration types, s^2, sp, sd, sf, p^2, pd, pf, d^2, df, f^2, have been identified and almost all of the terms arising from each.

The analyses of all three spectra are supported by measurements of Zeeman effects, which are interpreted with the aid of Landé's theory. The splitting factors (g values) for many levels show marked departure from the theoretical values, but the "g-sum rule" is valid wherever it is tested.

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I. INTRODUCTION

After the analyses of the arc and spark spectra of scandium [2] (Sc, Z=21) and yttrium [3] (Y, Z=39) had been published the authors decided to continue cooperation on the remaining spectra of this type. Lanthanum (La, Z=57) is a chemical analogue of scandium and yttrium; it occupies the same position in the third long period of elements that the former do in the first and second long periods, respectively. The fact that lanthanum occupies a position in the periodic system just preceding the group of 14 elements commonly called "rare earths" makes a complete analysis of its spectra of exceptional interest. Indeed, this analysis shows (vide infra) that the

[1] Professor of astronomy, Princeton University.
[2] H. N. Russell and W. F. Meggers, B. S. Sci. Paper No. 558, vol. 22, p. 329, 1927.
[3] W. F. Meggers and H. N. Russell, B. S. Jour. Research, vol. 2 (RP55), p. 733, 1929.

atom building process which accounts for the rare earth elements is actually anticipated in the electron configurations of the lanthanum atom. Furthermore, the exact nature of electron coupling in complex atoms like La, as disclosed by the analysis of spectral structure, is certain to be important in the further development of theory. In the present paper the authors give the results of an extensive analysis of lanthanum spectra in practically the same form as their results for scandium and yttrium; the summary of spectral theory given in the earlier publications applies also to the present case, and the notation is the same except for slight changes which bring it into conformity with the standardized nomenclature [4] and practice.

In 1914, Popow [5] published the first suggestion of regularities in lanthanum spectra. From Zeeman effect observations, he recognized six La lines as comprising a combination of triplet P and triplet D terms. In the same year Paulson [6] published a list of constant differences occurring between wave numbers corresponding to La spark lines, but no attempt was made to interpret the regularities. Even earlier, Rybar [7] had made extensive measurements of the Zeeman effects in La spectra and many complex patterns were published, but there was at that time no satisfactory explanation for most of these. Another decade passed before the theory of complex Zeeman effects began to unfold itself in the work of Landé,[8] thus paving the way for an explanation of the La observations. An attempt was made in 1924 by Goudsmit [9] who identified additional Paulson terms in the La II spectrum with the aid of Rybar's Zeeman effects. From the latter observations the Landé g values and quantum numbers j and l were derived for 20 energy levels accounting for approximately 70 lines.

In the following year the theory of spectral terms as developed by Heisenberg [10] and by Hund [11] gave some important suggestions as to the structures of La spectra and attempts were made by one of us to extend the analysis of the La II spectrum and also to find regularities in the La I spectrum. These efforts succeeded with the availability of new empirical data consisting of a description of La lines with respect to their behavior with temperature in the electric furnace by King and Carter [12] and of unpublished Zeeman effects kindly advanced by Prof. B. E. Moore. The temperature classification gave a reliable separation of La I and La II lines, and the new observations of Zeeman effects, especially in the red portion of the spectrum, gave the first clue to regularities in the La I spectrum. In addition to the 20 levels identified by Goudsmit, 22 more were found for La^+ atoms and combinations of these 42 levels accounted for about 180 La II lines.[13] For neutral La atoms 48 energy levels were found and their combinations accounted for about 130 lines.[14] In both cases the normal states or lowest energy levels were identified without ambiguity, but in each spectrum many lines remained unclassified, and many theoretical terms were still undiscovered. These preliminary analyses indicated

[4] H. N. Russell, A. G. Shenstone, and L. A. Turner, Phys. Rev., vol. 33, p. 900, 1929.
[5] S. Popow, Ann. d. Physik., vol. 45, p. 147, 1914.
[6] E. Paulson, Ann. d. Physik., vol. 45, p. 1203, 1914.
[7] S. Rybar, Phys. Zeit. vol. 12, p. 889, 1911.
[8] A. Landé, Zeit. f. Physik., vol. 15, p. 189, 1923; vol. 16, p. 391, 1923; vol. 19, p. 112, 1923.
[9] S. Goudsmit, Kon. Akad. Wet. Amsterdam, vol. 33, No. 8, p. 774, 1924.
[10] W. Heisenberg, Zeit. f. Physik., vol. 32, p. 841, 1925.
[11] F. Hund, Zeit. f. Physik., vol. 33, p. 345, 1925. Linienspektren und periodisches system der Elemente, Julius, Springer, Berlin, 1927.
[12] A. S. King and E. Carter, Astrophys. J., vol. 65, p. 86, 1927.
[13] W. F. Meggers, J. Opt. Soc. Am., vol. 14, p. 191, 1927.
[14] W. F. Meggers, J. Wash. Acad. Sci., vol. 17, p. 25, 1927.

that it would be impossible to extend them without still further experimental data,[15] so it was decided to make an entirely new description of La spectra. Such a description was recently completed by one of us,[16] and it serves as a basis for the analyses of La spectra to be detailed in the present paper. In addition to new wave-length determinations for more than 1,500 La lines in the interval 2,100 to 11,000 A, the new data include intensity estimates of arc and spark lines, separating them into three classes, La I, La II, and La III spectra, and improved observations of Zeeman effects for 460 lines ranging from 2,700 to 7,500 A. These data have permitted us to classify almost all of the lines ascribed to lanthanum atoms, to identify a large majority of the spectral terms, and correlate them with electron configurations. In each case it has been possible to recognize series-forming terms, the extrapolation of which lead to calculated ionization potentials of 5.59 volts for neutral La atoms, 11.38 volts for La^+ atoms, and 19.1 volts for La^{++} atoms. The total numbers of classified lines in the successive spectra are as follows: 540 for La I, 728 for La II, and 10 for La III.

On account of the greater complexity of La spectra, as compared with Sc and Y, and pronounced departures from theoretical interval ratios, line intensities and Zeeman effects, their analysis has been attended by greater difficulties and uncertainties, but patience and perseverance have been rewarded by the final classification of practically all lines without ambiguity. The detailed results will be presented for La III, then for La II, and finally for La I, thus proceeding from the relatively simple (alkali) case of 1-valence electron to the 2-electron spectrum with greatly increased transition possibilities and lastly to the spectrum characteristics of atoms with a full complement of 3-valence electrons.

II. THE SPECTRUM OF DOUBLY IONIZED LANTHANUM (La III)

Lanthanum belongs to the third long period in which electron orbits of the types $6s$, $6p$, and $5d$ are successively added to the completed xenon shell. Only one valence electron remains in doubly ionized lanthanum and in the normal state this electron is in a $5d$ orbit which produces a ^2D term. The next lowest state occurs with the $6s$ orbit, and higher states arise from $6p$, $6d$, $7s$ orbits. Some of these terms were already identified by Gibbs and White [17] and recently Badami [18] classified eight lines of the La III spectrum.

The new description of La spectra yielded 10 lines which are characterized by an enormous intensity difference between arc and spark and are, therefore, ascribed to doubly ionized atoms. Analysis of these data resulted in the identification of spectral terms listed in Table 1; the observed lines and estimated relative intensities appear in Table 2.

The observed and theoretical (Landé) splitting factors (g) are compared in the last column of the term table. Since La spectra possess g values which depart more or less from Landé, the observed Zeeman effects in the table of classified lines are compared with those computed from observed rather than theoretical g's. This procedure shows in

[15] W. F. Meggers, J. Wash. Acad. Sci., vol. 17, p. 35, 1927.
[16] W. F. Meggers, B. S. Jour. Research, vol. 9 (RP468), p. 239, 1932.
[17] R. C. Gibbs and H. E. White, Proc. Nat. Acad. Sci., vol. 12, p. 557, 1926; Phys. Rev., vol. 33, p. 157 1929.
[18] J. S. Badami, Proc. Roy. Soc. London, vol. 43, p. 53, 1931.

the first table, the deviations of observed from theoretical g values, and in the second table how closely the observed data are represented by the empirical g values. The observed or computed Zeeman patterns may be compared with the theoretical by reference to "Tables of Theoretical Zeeman Effects" published by Kiess and Meggers.[19] These remarks apply to the La II and La I spectra (vide infra) as well as to La III.

TABLE 1.—*Terms in the La III spectrum*

Electron configuration	Terms	Levels	Separations	g	
				Observed	Landé
	$5^3D_{1\frac{1}{2}}$	0.00	1,603.23		
$5d$	$5^3D_{2\frac{1}{2}}$	1,603.23			
$6s$	$6^3S_{1\frac{1}{2}}$	13,590.76		2.10	2.000
	$6^3P_1^0{}_{1\frac{1}{2}}$	42,014.92	3,095.72	.63	.667
$6p$	$6^3P_1^0{}_{2\frac{1}{2}}$	45,110.64		1.37	1.333
	$6^3D_{1\frac{1}{2}}$	82,378.75	433.76		
$6d$	$6^3D_{2\frac{1}{2}}$	82,812.51			
$7s$	$7^3S_{1\frac{1}{2}}$	82,345.0			

It will be shown later that the terms arising from the $4f$ electron are higher than those from $6p$ in La I, but lower in La II. This suggested that the La III combinations $5d$ (^{2}D)—$4f$ (^{2}F) might lie in the infra-red. The La spark spectrum in the interval 8,000 to 10,500 A was recently explored with xenocyanine plates, but no La III lines were found although La II lines were recorded all the way to 9,893.8 A.

TABLE 2.—*Classified lines in the La III spectrum*

λ(air) I. A.	Intensity	ν(vac) cm^{-1}	Term combinations	Zeeman effect	
				Observed	Computed
3,517.14	200	28,424.09	$6^3S_{1\frac{1}{2}}$—$6^3P_0^0{}_{1\frac{1}{2}}$	(0.73)1.36	(0.74)1.36
3,171.68	300	31,519.94	$6^3S_{1\frac{1}{2}}$—$6^3P_1^0{}_{1\frac{1}{2}}$	(0.37)0.99, 1.76	(0.36)1.00, 1.74
2,684.90	50	37,234.29	$6^3P_1^0{}_{1\frac{1}{2}}$—$7^3S_{1\frac{1}{2}}$		
2,682.46	30	37,268.16	$6^3P_1^0{}_{1\frac{1}{2}}$—$6^3D_{1\frac{1}{2}}$		
2,651.60	300	37,701.87	$6^3P_1^0{}_{1\frac{1}{2}}$—$6^3D_{2\frac{1}{2}}$		
2,478.8[1]	20	40,329.9	$6^3P_0^0{}_{1\frac{1}{2}}$—$7^3S_{1\frac{1}{2}}$		
2,476.72	100	40,363.79	$6^3P_0^0{}_{1\frac{1}{2}}$—$6^3D_{1\frac{1}{2}}$		
2,379.38	200	42,014.92	$5^3D_{1\frac{1}{2}}$—$6^3P_0^0{}_{1\frac{1}{2}}$		
2,297.75	200	43,507.40	$5^3D_{2\frac{1}{2}}$—$6^3P_1^0{}_{1\frac{1}{2}}$		
2,216.08	50	45,110.63	$5^3D_{1\frac{1}{2}}$—$6^3P_1^0{}_{1\frac{1}{2}}$		

[1] Near carbon line, 2,478.6 A.

III. THE SPECTRUM OF SINGLY IONIZED LANTHANUM (La II)

The spark spectrum of lanthanum is exceptionally complex; more than 800 lines appearing in spark spectrograms are associated with La^+ atoms. Superficially, the lanthanum spark spectrum resembles the yttrium spark spectrum; in each case the lines are divided roughly into two classes by comparison of arc and spark spectrograms. One

[19] C. C. Kiess and W. F. Meggers, B. S. Jour. Research, vol. 1 (RP23), p. 64, 1928.

group, including most of the stronger lines, has nearly the same appearance in a 6-ampere, 220-volt arc and in a high voltage condensed discharge, while the second, lying mainly in the ultra-violet, is greatly enhanced upon passing from the arc to the spark and consists largely of hazy and unsymmetrical lines. The former arise from combinations of low energy states with the next higher or middle set, while the latter are practically all identified as combinations of middle terms with a still higher third set.

The lowest energy states which can arise from s and d type electrons are identified with (even) spectral terms as follows:

Electron configuration	Spectral terms
s^2	^1S
sd	^1D ^3D
d^2	$^1S,^1D,^1G$ ^3P ^3F

All of these have been identified except $(d^2)^1S$. Which particular term will be the lowest energy and represent the normal state of the atom depends on the relative strength of binding of the individual electrons. It is very remarkable that the homologous atoms, Sc^+, Y^+, and La^+, each make a different choice; the normal state of Sc^+ is $(sd)^3D$, of Y^+ $(s^2)^1S$, and of La^+ $(d^2)^3F$.

Substitution of a p electron for an s or a d electron produces the following set of (odd) middle terms:

Electron configuration	Spectral terms
sp	^1P ^3P
dp	$^1P,^1D,^1F$ $^3P,^3D,^3F$

All of the easily excited lines of Sc^+ and Y^+ are accounted for by the above-mentioned low and middle spectral terms, but in the case of La^+ a large number of otherwise superfluous lines indicate additional middle-set terms to account for which it is necessary to conclude that f-type electrons are present. Thus, the substitution of f- for p-type electrons would yield the following additional (odd) middle-set terms:

Electron configuration	Spectral terms
sf	^1F ^3F
df	$^1P,^1D,^1F,^1G,^1H$ $^3P,^3D,^3F,^3G,^3H$

All of these terms have been found in the La II spectrum, they increase the number of middle-set levels from 16 to 40 and thus account for the greater complexity of the spectrum.

The terms produced by the $4f$ electrons lie lower than those arising from the $6p$. This is obviously related to the fact that $4f$ electrons are bound into the normal state of the directly following elements, Ce to Lu, while the $6p$ electrons begin to be similarly bound only in Tl. In Ba I the f electron is much more loosely bound than the p. There are numerous high even terms in La II. Those arising from the configurations $5d\ 7s$, $5d\ 6d$, $6s\ 6d$, and $6p^2$ are homologous with similar terms in Sc II and Y II. Two important additional groups evidently arise from $6p\ 4f$ and $4f^2$. The former are the lowest of all the high even terms. Some hazy lines confined to the spark appear to be combinations between these and still higher odd levels which have been denoted by numbers 1° to 8°. There are several configurations (for example, $5d\ 7p$, $5d\ 5f$, $6p\ 6d$, $4f\ 6d$) which may give rise to levels of this sort, and they must be very numerous. They should combine with the ground terms to give lines in the

Schumann region. Observations in this region may detect many more such levels and thus lead to the interpretation of the remaining unclassified lines in the visible and near ultra-violet.

This is the most completely developed example of a 2-electron spectrum which has yet been investigated. All the configuration types, s^2, sp, sd, sf, p^2, pd, pf, d^2, df, f^2, have been identified and almost all of the terms arising from each. The theoretical relations of the terms arising from each configuration have been discussed by Condon and Shortley.[20] The agreement of the observed and computed levels is, in general, good, and their theoretical predictions led to the correct identification of the difficult terms $(df)^1H$ and $(f^2)^1I$.

The terms which have been identified in the La II spectrum are listed in Table 3, in which term symbols, relative values of the levels, level separations, adopted and Landé g values, and combining terms are given in successive columns. The adopted g values are derived from the observed Zeeman effects for La II lines starting with the completely resolved patterns and then applying the formulas of Shenstone and Blair[21] to the unresolved blends. For patterns which though unresolved had perpendicular (n) components distinctly shaded outwards (A^1) or inwards (A^2) the attempt was made to measure the points of maximum intensity corresponding to the strongest components. If x is the observed separation we should then have

$$x = J_1 g_1 - J_2 g_2 \quad (J_1 = J_2 + 1) \tag{1}$$

When no such asymmetry was noticed it was assumed that the settings were on the centroid of the whole pattern and the formula then used was

$$2x = (J_1 + 1) g_1 - J_2 g_2 \tag{2}$$

When $J_1 = J_2$ the equations are

$$2\,x = g_1 + g_2 \ (n \text{ components}) \tag{3}$$

$$4/3y = (J + 1/2)\ (1 - X)\ (g_1 - g_2) \quad (p \text{ components}) \tag{4}$$

where $X = \dfrac{1}{(2J+1)^2}$ or $\dfrac{1}{4J\,(J+1)}$ according as J is integral or half integral.[22]

The weights assigned to the adopted g's in Table 3 depend on the number and consistency of the derived values. The probable error corresponding to unit weight is ± 0.020.

Most of the g's have nearly the theoretical (Landé) values but marked discrepancies frequently appear which may be attributed to deviations of the actual coupling of the vectors from the ideal SL coupling for narrow multiplets. Some of the largest discordances are clearly due to "g sharing" among neighboring levels with the same J; for example, e^3G_4, e^3F_4; y^3D_1, y^3P_1, z^1P_1. In these cases the intensities of many combinations are also abnormal.

[20] E. U. Condon and C. H. Shortley, Phys. Rev., vol. 37, p. 1025, 1931.
[21] A. G. Shenstone and H. A. Blair, Phil. Mag., vol. 8, p. 765, 1929.
[22] H. N. Russell, Phys. Rev., vol. 36, p. 1590, 1930.

TABLE 3.—*Relative terms in the La II spectrum*

Electron configuration	Term	Level	Level separations	g		Combinations
				Adopted weight	Landé	
$5d^2$	a^3F_2	0.00	1,016.10	0.730 7½	0.667	z^3F°, z^1F°, z^1G°, y^3F°, z^3H°, z^1D°, z^3G°, z^3D°, z^3P°, y^1D°, y^1F°, y^3D°, x^3F°, z^1P°, y^3P°, z^3P°, x^1F°, x^1P°.
	a^3F_3	1,016.10	954.60	1.092 9	1.083	
	a^3F_4	1,970.70		1.258 8	1.250	
$6s5d$	a^1D_2	**1,394.46**		.987 10½	1.000	z^3F°, z^1F°, y^3F°, z^1D°, z^3G°, z^3D°, z^3P°, y^1D°, y^1F°, y^3D°, x^3F°, z^1P°, y^3P°, y^1P°, x^3P°, z^1F°, x^1P°.
$6s5d$	a^3D_1	1,895.15	696.45	.520 13	.500	z^3F°, z^1G°, y^3F°, z^3H°, z^1D°, z^3G°, z^3D°, z^3P°, y^1D°, y^1F°, y^3D°, x^3F°, z^1P°, y^3P°, y^1P°, z^3P°, x^1F°, x^1P°.
	a^3D_2	2,591.60	658.75	1.140 8	1.167	
	a^3D_3	3,250.35		1.337 11	1.333	
$5d^2$	a^3P_0	5,249.70	468.42	0/0 6	0/0	y^3F°, z^1D°, z^3D°, z^3P°, y^1D°, y^1F°, y^3D°, x^3F°, z^1P°, y^3P°, y^1P°, x^3P°, x^1F°, x^1P°.
	a^3P_1	5,718.12	509.30	1.506 9	1.500	
	a^3P_2	6,227.42		1.488 11½	1.500	
$6p^2$	a^1S_0	7,394.57		0/0 4	0/0	z^3D°, z^3P°, y^1D°, z^1P°, y^1P°, x^3P°, x^1P°.
$5d^2$	a^1G_4	7,473.32		1.003 2	1.000	z^1G°, y^3F°, z^3H°, z^3G°, z^3D°, y^1F°, y^3D°, x^3F°, z^3H°, x^1F°.
$5d^2$	b^1D_2	10,094.86		1.015 70	1.000	z^3D°, z^3P°, y^1D°, y^3D°, x^3F°, z^1P°, y^3P°, y^1P°, x^3P°, x^1F°, x^1P°.
$6s4f$	$z^3F_2^\circ$	14,147.98	227.19	.676 7	.667	a^3F, a^1D, a^3D, e^3G, e^3F, e^1F, e^3D, e^1G, f^1D, f^1F, f^3G, f^3F, g^3D, e^3H, g^3F, h^1D.
	$z^3F_3^\circ$	14,375.17	323.57	1.087 10	1.083	
	$z^3F_4^\circ$	15,698.74		1.258 9	1.250	
$6s4f$	$z^1F_3^\circ$	15,773.77		1.047 10	1.000	a^3F, a^1D, e^3G, e^3F, e^1F, e^3D, e^1G, e^1D, f^1D, f^3G, f^3F, g^3D, f^1G, e^3H, f^3F, h^1D, e^3D, i^1D.
$5d4f$	$z^1G_4^\circ$	16,599.17		.996 4	1.000	a^3F, a^3D, a^1G, e^3G, e^3F, e^1F, e^1G, f^1F, f^3G, f^1G, e^3H, g^3F, g^1G.
$5d4f$	$y^3F_2^\circ$	17,211.93	1,023.63	.757 8	.667	a^3F, a^1D, a^3D, a^3P, a^1G, e^3G, e^3F, e^3D, e^1G, e^1D, f^1D, f^1F, f^3G, g^3D, f^1G, g^3F, g^1G, h^1D, f^3P, i^1D.
	$y^3F_3^\circ$	18,235.56	978.98	1.090 8	1.083	
	$y^3F_4^\circ$	19,214.54		1.243 6	1.250	
$5d4f$	$z^3H_4^\circ$	17,825.62	754.79	.865 2	.800	a^3F, a^3D, a^1G, e^3G, e^3F, e^1F, e^1G, f^3F, f^1G, e^3H g^3F, g^1G, e^1I.
	$z^3H_5^\circ$	18,580.41	1,169.21	1.082 4	1.033	
	$z^3H_6^\circ$	19,749.62		1.17 1	1.167	
$5d4f$	$z^1D_2^\circ$	18,895.41		.931 3½	1.000	a^3F, a^1D, a^3D, a^3P, e^3G, e^3F, e^1F, e^3D, e^1D, f^3D, f^1F, f^3G, f^3F, g^3D, e^1P, e^3S, g^3F, h^1D, g^3P, h^3D, f^3P, i^1D.
$5d4f$	$z^3G_3^\circ$	20,402.82	928.78	.775 4	.750	a^3F, a^1D, a^3D, a^1G, e^3G, e^3F, e^1F, e^3D, e^1D, f^1G, f^3F, g^1D, f^1G, e^3H, g^3F, g^1G.
	$z^3G_4^\circ$	21,331.60	951.30	1.060 6	1.050	
	$z^3G_5^\circ$	22,282.90		1.203 5	1.200	
$5d4f$	$z^3D_1^\circ$	21,441.73	664.29	.547 8	.500	a^3F, a^1D, a^3D, a^3P, a^1S, a^1G, b^1D, e^3G, e^3F, e^1F, e^3D, e^1G, e^1D, f^3D, f^1D, f^3G, f^3F, g^3D, e^1P, e^3S, e^3P, g^1D, f^1G, e^3H, g^3F, h^1D, g^3P, f^3P, i^1D.
	$z^3D_2^\circ$	22,106.02	431.28	1.186 12	1.167	
	$z^3D_3^\circ$	22,537.30		1.317 10	1.333	
$5d4f$	$z^3P_0^\circ$	22,683.70	21.45	0/0	0/0	a^3F, a^1D, a^3D, a^3P, a^1S, b^1D, e^3D, e^1D, f^3D, f^1F, g^1D, e^1P, e^3S, e^3P, g^1D, g^3F, h^1D, g^3P, h^3D, f^3P, i^1D.
	$z^3P_1^\circ$	22,705.15	541.78	1.458 7	1.500	
	$z^3P_2^\circ$	23,246.93		1.462 7	1.500	
$6p\ 5d$	$y^1D_2^\circ$	24,462.66		.897 7½	1.000	a^3F, a^1D, a^3D, a^3P, b^1D, e^3G, e^3D, f^3D, f^1D, f^1F, f^3G, f^3F, y^3D, e^1P, e^3P, h^1D, f^3P, i^1D.
$5d4f$	$y^1F_3^\circ$	24,522.70		1.032 8	1.000	a^3F, a^1D, a^3D, a^3P, a^1G, e^3G, e^1F, e^3D, e^1G, e^1D, f^1F, g^3D, g^1G, h^1D, g^3P, f^3P, i^1D.
$6p\ 5d$	$y^3D_1^\circ$	25,973.37	1,414.74	.799 8	.500	a^3F, a^1D, a^3D, a^3P, a^1S, a^1G, b^1D, e^3F, e^3D, e^1D, f^3D, f^1G, f^3F, g^3D, e^1P, e^3S, e^3P, g^1D, f^1G, e^3H, h^1D, g^3P, h^3D, f^3P, i^1D.
	$y^3D_2^\circ$	27,388.11	927.14	1.191 10	1.167	
	$y^3D_3^\circ$	28,315.25		1.312 7	1.333	
$6p\ 5d$	$z^3F_2^\circ$	26,414.01	423.65	.836 7½	.667	a^3F, a^1D, a^3D, a^3P, a^1G, b^1D, e^3G, e^3F, e^1F, e^3D, e^1D, f^3D, f^1D, f^1F, f^3G, f^3F, g^3D, e^1P, e^3S, g^1D, f^1G, e^3H, h^1D, g^3P, i^1D, i^3D.
	$z^3F_3^\circ$	26,837.66	1,727.74	1.081 6	1.083	
	$z^3F_4^\circ$	28,565.40		1.246 4	1.250	
$5d4f$	$z^1P_1^\circ$	27,423.91		.882 9	1.000	a^3F, a^1D, a^3D, a^3P, a^1S, b^1D, e^1D, f^3D, f^1D, e^1P, e^3S, e^3P, e^1S, g^3P, g^1S, h^3D, f^3P, i^1D, f^1S.
$5d4f$	$z^1H_5^\circ$	28,525.71		1.00 1	1.000	a^1G, e^1G, e^1H, g^1G, e^1I.
$6p\ 5d$	$y^3P_0^\circ$	27,545.85	608.70	0/0	0/0	a^3F, a^1D, a^3D, a^3P, b^1D, e^3D, f^3D, f^1D, g^3D, e^3S, e^3P, g^1D, g^3P, g^1S, h^3D, f^3P, i^1D, f^1S.
	$y^3P_1^\circ$	28,154.55	1,343.50	1.262 5	1.500	
	$y^3P_2^\circ$	29,498.05		1.495 5	1.500	
$6p\ 5d$	$y^1P_1^\circ$	30,353.33		1.066 6	1.000	a^1D, a^3D, a^3P, b^1D, e^1D, f^1D, f^1F, e^1P, e^3P, e^1S, g^1S, h^3D, i^1D, f^1S, ^1D?
$5s\ 6p$	$z^3P_0^\circ$	31,785.82	375.17	0/0	0/0	a^3F, a^1D, a^3D, a^3P, e^1S, b^1D, f^3G, g^3D, e^1P, e^3S, e^1S, g^3P, h^3D, f^3P.
	$z^3P_1^\circ$	32,160.99	1,043.42	1.515 6	1.500	
	$z^3P_2^\circ$	33,204.41		1.478 4	1.500	
$6p\ 5d$	$z^1F_3^\circ$	32,201.05		1.006 7	1.000	a^3F, a^1D, a^3D, a^3P, a^1G, b^1D, f^3D, f^1D, f^1F, f^3G, f^1G, g^3F, g^1G, h^1D, i^1D, ^1D?
$6p\ 4f$	e^3G_3	35,452.66	1,720.13	.873 5	.750	z^3F°, z^1F°, z^1G°, y^3F°, z^3H°, z^1D°, z^3G°, z^3D°, y^1D°, y^1F°, z^1P°.
	e^3G_4	37,172.79	1,845.95	1.146 7	1.050	
	e^3G_5	39,018.74		1.203 3	1.200	
$6p\ 4f$	e^3F_2	35,787.53	1,167.12	.732 5	.667	z^3F°, z^1F°, z^1G°, y^3F°, z^3H°, z^1D°, z^3G°, z^3D°, y^1D°, x^3F°.
	e^3F_3	36,954.65	835.92	1.061 7½	1.083	
	e^3F_4	37,790.57		1.141 7	1.250	
$6p\ 4f$	e^1F_3	37,209.71		.953 6	1.000	z^3F°, z^1F°, z^1G°, z^3H°, z^1D°, z^3G°, z^3D°, y^1F°, x^3F°.
$6p\ 4f$	e^1G_4	39,221.65		1.060 6	1.000	z^3F°, z^1F°, z^1G°, y^3F°, z^3H°, z^3G°, z^3D°, y^1F°, z^1H°.

TABLE 3.—*Relative terms in the La II spectrum*—Continued

Electron configuration	Term	Level	Level separations	g			Combinations
				Adopted weight		Landé	
6p 4f	e^3D_1	38,534.11	−312.62	0.495	6	0.500	$z^3F°$, $z^1F°$, $z^3F°$, $z^1D°$, $z^3G°$, $z^3D°$, $z^3P°$, $y^1D°$
	e^3D_2	38,221.49		1.100	7	1.167	$y^1F°$, $y^3D°$, $z^3F°$, $y^3P°$.
	e^3D_3	39,402.55	1,181.06	1.306	9	1.333	
6p 4f	e^1D_2	40,457.71		1.046	5	1.000	$z^1F°$, $y^3F°$, $z^1D°$, $z^3G°$, $z^3D°$, $z^3P°$, $y^1F°$, $y^3D°$, $z^3F°$, $y^1P°$.
6s 6p	$z^1P_1^?$	45,692.17		.97	1	1.000	a^3F, a^1D, a^3D, a^3P, a^1S, b^1D, i^1D.
5d 7s	f^3D_1	49,733.13		.520	3	.500	$z^3F°$, $z^1D°$, $z^3D°$, $z^3P°$, $y^1D°$, $y^3D°$, $z^3F°$, $z^1P°$, $^3yP°$, $z^1F°$.
	f^3D_2	49,884.35	151.22	1.141	3½	1.167	
	f^3D_3	51,228.57	1,344.22	1.331	3	1.333	
5d 7s	f^1D_2	51,523.86		1.02	1½	1.000	$z^1F°$, $y^3F°$, $z^3D°$, $y^1D°$, $x^3F°$, $z^1P°$, $y^3P°$, $y^1P°$, $x^1F°$.
5d 6d	f^1F_3	52,137.67		1.00	1	1.000	$z^3F°$, $z^1G°$, $y^3F°$, $z^1D°$, $z^3P°$, $y^1D°$, $y^1F°$, $z^3F°$, $x^1F°$.
5d 6d	f^3G_3	52,857.88		.89	1	.750	$z^3F°$, $z^1F°$, $z^1G°$, $y^3F°$, $z^3G°$, $x^3F°$, $x^1F°$.
	f^3G_4	53,333.37	475.49	1.05	1	1.050	
	f^3G_5	54,434.65	1,101.28	1.20	1	1.200	
5d 6d	f^3F_2	53,885.24		.77	2	.667	$z^3F°$, $z^1F°$, $z^3H°$, $z^1D°$, $z^3G°$, $z^3D°$, $y^1D°$, $y^3D°$, $z^3F°$.
	f^3F_3	54,840.04	954.80	1.14	2	1.083	
	f^3F_4	55,321.35	481.31	1.16	2	1.250	
5d 6d	g^3D_1	52,169.66		.67	3	.500	$z^1F°$, $y^3F°$, $z^1D°$, $z^3D°$, $z^3P°$, $y^1D°$, $y^1F°$, $y^3D°$, $x^3F°$, $y^3P°$, $z^3P°$.
	g^3D_2	52,734.81	565.15	1.17	1	1.167	
	g^3D_3	53,689.56	954.75	1.21	3	1.333	
5d 6d	e^3S_1	54,365.80		1.42	1	2.000	$z^1D°$, $z^3D°$, $z^3P°$, $y^3D°$, $x^3F°$, $z^1P°$, $y^3P°$, $y^1P°$, $x^3P°$.
5d 6d	e^1P_1	53,302.56					$z^1D°$, $z^3D°$, $z^3P°$, $y^1D°$, $y^3D°$, $x^3F°$, $z^1P°$, $y^1P°$, $x^3P°$.
5d 6d	e^3P_0	54,964.19?					
	e^3P_1	55,230.33	236.14	1.57	1	1.500	$z^3D°$, $z^3P°$, $y^1D°$, $y^3D°$, $z^1P°$, $y^3P°$, $y^1P°$.
	e^3P_2	56,036.60	806.27	1.22	1	1.500	
5d 6d	f^1G_4	56,035.70		1.03		1.000	$z^1F°$, $z^1G°$, $y^3F°$, $z^3H°$, $z^3G°$, $z^3D°$, $y^3D°$, $z^3F°$, $x^1F°$.
5d 6d	$g^1{}_1D_2$	55,184.05		1.08	1	1.000	$z^3G°$, $z^3D°$, $z^3P°$, $y^3D°$, $x^1F°$, $y^3P°$.
5d 6d	e^1S_0	54,793.82					$z^1P°$, $z^3P°$.
$4f^2$	e^3H_4	55,107.25		.94	1	.800	$z^3F°$, $z^1F°$, $z^1G°$, $z^3H°$, $z^3G°$, $z^3D°$, $y^3D°$, $z^1F°$, $z^1H°$.
	e^3H_5	55,982.09	874.84	1.04	2	1.033	
	e^3H_6	56,837.94	855.85	1.18	1	1.167	
$4f^2$	g^3F_2	57,399.58					z^3F, $z^1F°$, $z^1G°$, $y^3F°$, $z^3H°$, $z^1D°$, $z^3G°$, $z^3D°$, $z^3P°$, $z^1F°$.
	g^3F_3	57,918.50	518.92	1.11	1	1.083	
	g^3F_4	58,259.41	340.91	1.22	1	1.250	
$4f^2$	g^1G_4?	59,527.60		1.07	1	1.000	$z^1G°$, $y^1F°$, $z^3H°$, $z^3G°$, $y^1F°$, $z^1H°$, $x^1F°$.
$4f^2$	h^1D_2	59,900.08		1.00	1	1.000	$z^3F°$, $z^1F°$, $y^3F°$, $z^1D°$, $z^3D°$, $z^3P°$, $y^1D°$, $y^1F°$, $y^3D°$, $x^3F°$, $x^1F°$.
$6p^2$	$f^3P_0^3$	60,094.84		0/0		0/0	
	f^3P_1	61,128.83	1,033.99	1.47	1½	1.500	$y^3F°$, $z^1D°$, $z^3D°$, $z^3P°$, $y^1D°$, $y^1F°$, $y^3D°$, $z^3P°$, $y^3P°$, $z^3P°$.
	f^3P_2	62,506.36	1,377.53	1.45	1½	1.500	
$6p^2$	f^1D_2	62,026.27					$z^1F°$, $y^3F°$, $z^1D°$, $z^3D°$, $z^3P°$, $y^1D°$, $y^1F°$, $z^1F°$, $z^1P°$, $y^3P°$, $y^1P°$, $x^1F°$, $x^1P°$.
$4f^2$	e^1I_6	62,408.40		1.01	1	1.000	z^3H^3, $z^1H°$.
$4f^2$	g^3P_0	63,463.95					$z^1D°$, $z^3D°$, $z^3P°$, $y^1F°$, $y^3D°$, $x^3F°$, $z^1P°$, $y^3P°$, $x^3P°$.
	g^3P_1	63,703.18	239.23				
	g^3P_2	64,278.92	575.74				
6s 6d	h^3D_1	64,361.23					$z^1D°$, $z^3P°$, $y^3D°$, $z^1P°$, $y^3P°$, $y^1P°$, $x^3P°$.
	h^3D_2	64,529.90	168.62				
	h^3D_3	64,692.59	162.69				
	$^1D_2^?$	64,706.76?					$y^1P°$, $x^1F°$.
$6p^2$	f^1S_0	66,591.91					$z^1P°$, $y^3P°$, $y^1P°$.
$4f^2$	g^1S_0	69,505.06					$z^1P°$, $y^3P°$, $y^1P°$.
6d 6s	i^3D_3	69,233.90					$y^3D°$, $x^3F°$.
	$1i_4^3$	57,364.12					e^3G, e^3F, e^3D.
	$2i_4^3$	58,748.90					e^3G, e^3F, e^1F.
	$3i_{4,3}^3$	59,612.64					e^3G, e^3F, e^3D.
	$4i_4^3$	60,744.17					e^3G, e^3D.
	$5i_{4,3}^3$	61,017.66					e^3F.
	$6i_{4,3}^1$	61,514.46					e^1F, e^1G.
	$7i_{4,3}^1$	63,598.87					e^3G, e^1G.
	$8i_4^1$	64,411.17					e^3G, e^1F, e^3D.

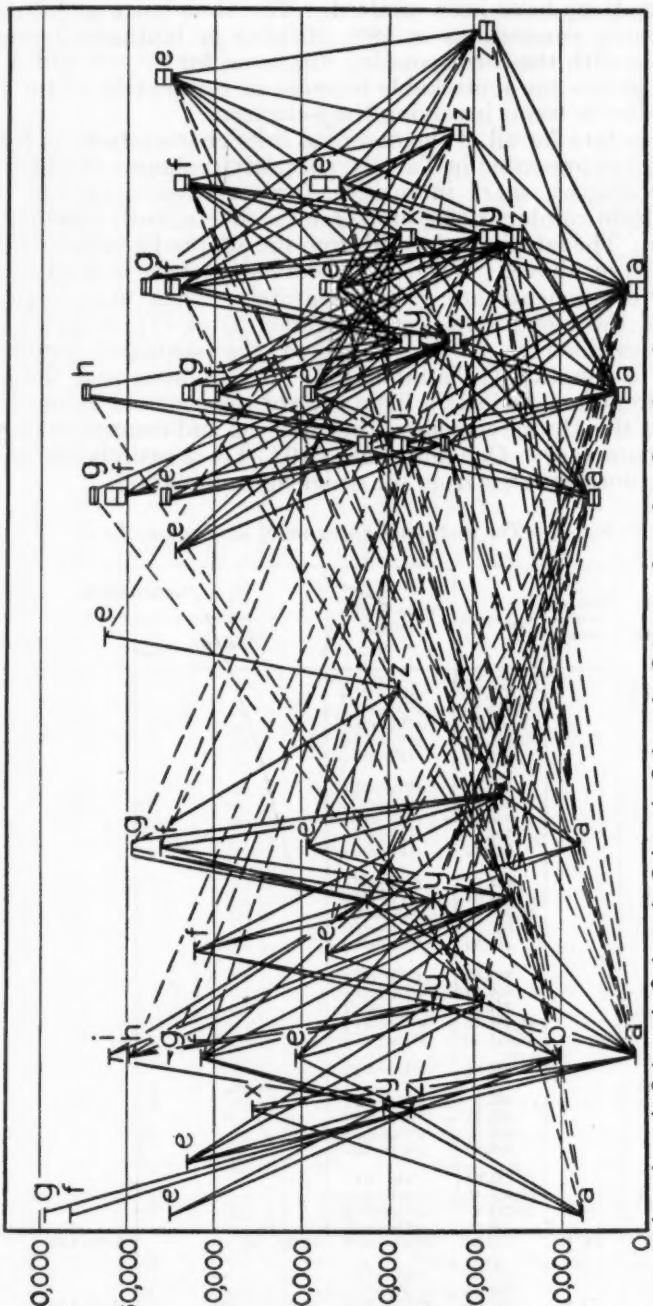

FIGURE 1.—*Terms and combinations in the La II spectrum*

A diagram of the La II terms and combinations is reproduced in Figure 1. In order to avoid making the figure too confusing some of the combinations have been omitted. The abundance and strength of intersystem connections is very striking in lanthanum spectra. Comparison with the corresponding diagrams for Sc II[23] and Y II[24] show at a glance the remarkable increase in complexity of the La II spectrum due to terms involving the *f*-electron.

Complete data for all of the observed lines characteristic of ionized lanthanum are presented in Table 4, successive columns of which contain wave lengths, spark intensities, furnace classes, vacuum wave numbers, term combinations, and Zeeman effects, both observed and computed. The latter are derived from the adopted *g* values with the formulas given above. When the observed pattern is resolved, the computed components are given separately; when unresolved, the centroid of the blend given by equations (2) or (4), except for the patterns described as A^1 or A^2, where the strongest component according to equation (1) is tabulated. In the latter case the measured position often deviates a little toward the centroid of the group. Apart from this the agreement of the observed and computed values is usually satisfactory. One faint line, 4,193.34 A is entirely discordant, and clearly does not arise from the assigned combination.

TABLE 4.—*The first spark spectrum of lanthanum (La II)*

λ_{air} I. A.	Intensity spark	Temperature class	ν_{vac} cm^{-1}	Term combinations	Zeeman effects	
					Observed	Computed
10, 954. 6	3		9, 126. 09	a^1G_4—$z^1G^\circ_4$		
10, 186. 5	2		9, 814. 2	$y^3D^\circ_1$—e^3F_2		
10. 093. 54	1		9, 904. 62	$y^3P^\circ_2$—e^3D_3		
9, 893. 82	4		10, 104. 55	$y^1P^\circ_1$—e^1D_2		
9, 672. 94	3		335. 29	$x^3F^\circ_3$—e^3G_4		
9, 657. 00	20		352. 35	a^1G_4—$z^3H^\circ_4$		
9, 563. 60	4		453. 45	$x^3F^\circ_4$—e^3G_5		
9, 346. 69	15		696. 04	$z^1H^\circ_5$—e^1G_4		
9, 260. 42	3		795. 69	$x^1F^\circ_3$—e^1F_3		
9, 146. 75	2		929. 85	$x^1F^\circ_3$—e^3G_3		
9, 127. 5	1		952. 9	$x^3F^\circ_3$—e^3F_4		
9, 101. 10	2		984. 67	a^3P_1—$y^3F^\circ_2$		
9, 096. 71	3		10, 989. 97	$y^1D^\circ_2$—e^1G_3		
9, 016. 80	2		11, 087. 37	$y^3D^\circ_3$—e^3D_3		
8, 810. 57	3		346. 89	f^1D_2—$z^1D^\circ_2$		
8, 781. 98	2		383. 83	$x^3F^\circ_3$—e^3D_3		
8, 650. 82	2		556. 43	a^3D_3—$z^3F^\circ_3$		
8, 514. 65	3		741. 24	a^1G_4—$y^3F^\circ_4$		
8, 484. 01	2		11, 783. 65	a^3D_2—$z^3F^\circ_3$		
8, 323. 35	1		12, 011. 10	b^1D_2—$z^3D^\circ_2$		
8, 159. 05	10? Spark.		252. 96	a^3D_1—$z^3F^\circ_2$		
8, 059. 5	3 h		404. 3	a^3F_4—$z^3F^\circ_4$		
7, 927. 83	2		610. 33	b^1D_2—$z^3P^\circ_1$		
7, 891. 69	2		668. 08	a^3P_2—$z^1D^\circ_2$		
79. 93	4		686. 98	$y^1F^\circ_3$—e^1F_3		
7, 838. 83	1		753. 50	a^1D_2—$z^3F^\circ_3$		
7, 740. 54	2 h		12, 915. 45	$z^3D^\circ_1$—e^3G_3		
7, 612. 94	3		13, 131. 92	a^3F_3—$z^3F^\circ_3$		
7, 489. 15	1		348. 98	a^3D_3—z^1G_4		
7, 483. 48	30	IV E	359. 10	a^3F_3—$z^3F^\circ_3$	(0.00) 1.12	(0.00) 1.09
7, 340. 08	2		620. 08	$x^3F^\circ_4$—e^1D_2		
7, 297. 99	2		698. 63	$y^1F^\circ_3$—e^3D_3		
82. 36	150	III E	728. 03	a^3F_4—$z^3F^\circ_4$	(0.00 w) 1.26	(0.00) 1.26
66. 13			758. 70	$y^1D^\circ_2$—e^3D_2		
7, 213. 95	2		13, 858. 22	a^1G_4—$z^3G^\circ_4$		

[23] See footnote 2, p. 625.

[24] See footnote 3, p. 625.

TABLE 4.—*The first spark spectrum of lanthanum (La II)*—Continued

λ_{air} I. A.	Intensity spark	Temperature class	ν_{vac} cm^{-1}	Term combinations	Zeeman effects	
					Observed	Computed
7,118.6	2		14,043.8	$x^3F_2^\circ - z^1D_2$		
16.8	3		047.4	$a^1S_0 - z^3D_1^\circ$		
7,104.7	3 h		071.3	$y^1D_2^\circ - e^3D_1$		
7,079.74	4		120.92	$z^3G_3 - e^3G_3$		
7,066.24	300	III E	147.90	$a^3F_2 - z^3F_2^\circ$	(0.00) 0.70	(0.00) 0.70
6,968.78	25	V E	345.76	$z^3D_1^\circ - e^3F_2$	(0.00) 0.81	(0.00) 0.82
58.11	100	IV E	367.76	$b^1D_2 - y^1D_2^\circ$	(0.21) 0.96	(0.21) 0.96
54.54	20	IV	375.14	$a^3F_2 - z^3F_3^\circ$		
52.52	10	IV	379.31	$a^1D_2 - z^1F_3^\circ$	(0.00) 1.10	(0.00) 1.11
6,902.08	3	III	484.40	$y^3D_1^\circ - e^1D_2$		
6,859.03	5	V	575.31	$a^3D_3 - z^3H_4^\circ$		
37.91	15	IV ? E	620.32	$a^3D_2 - y^3F_2^\circ$		
34.07	20	IV ? E	628.54	$a^3F_4 - z^1G_4^\circ$	(1.05) ?	(0.87) 1.13
30.83	6	V E	635.48	$z^3D_3^\circ - e^3G_4$	(0.00) 0.98	(0.00) 0.89
13.68	50	V ? E	672.32	$z^3D_2^\circ - e^1F_3$	(1.04) 1.29 B	(0.94) 1.14
08.88	30	IV	682.66	$a^3F_3 - z^1F_4^\circ$	(0.00 h) 1.56 h	(0.00) 1.51
6,801.38	5		698.85	$y^1F_3^\circ - e^1G_4$	(0.00) 1.10	(0.00) 1.10
6,774.28	100	III E	757.65	$a^3F_3 - z^1F_3^\circ$	(0.00 w) 1.10	(0.12) 1.07
50.47	1		809.70	$a^1G_4 - z^3G_5^\circ$		
32.80	40	V E	848.57	$z^3D_2^\circ - e^3F_3$	(0.00) 0.99	(0.00) 0.94
18.68	60	V E	879.78	$y^1F_3^\circ - e^3D_2$	(0.69) 1.12 B	(0.70) 1.17
6,714.08	80	V E	889.97	$z^3G_3^\circ - e^3G_4$	(0.00) 1.38	(0.00) 1.32
6,676.14	3		974.59	$z^3P_2^\circ - e^3D_2$		
71.41	40	IV ? E	14,985.20	$a^3D_2 - y^3F_2^\circ$	(0.63) 1.17	(0.64) 1.21
42.79	100	V E	15,049.77	$z^3G_3^\circ - a^3G_3$	(0.33) 0.82	(0.25) 0.82
36.53	5	V	063.96	$a^1G_4 - z^3D_3^\circ$		
6,619.10	2		103.63	$z^3D_2^\circ - e^1F_2$		
6,570.96	(?)	III	214.28	$a^3P_2 - z^3D_1^\circ$		
54.18	(?)	V	253.23	$z^3D_3^\circ - e^3F_4$		
29.72	4 h	III ?	310.37	$a^1S_0 - z^3P_1^\circ$		
6,526.99	200	III E	316.77	$a^3D_1 - y^3F_2^\circ$	(0.00, 0.22) 0.94 A^2	(0.00, 0.24) 0.52, 0.76, 0.99
6,498.19	250	IV ? E	384.66	$z^3G_3^\circ - e^3F_2$	(0.00) 0.81	(0.00) 0.82
46.62	200	V E	507.73	$z^3G_3^\circ - e^3F_4$	(0.00 w) 1.43 A^2	(0.00) 1.45 A^2
43.05	50 h	V	516.32	$z^3P_1^\circ - e^3D_2$	(0.00 w) 0.76 A^1	(0.00) 0.74 A^1
6,415.39	1		583.22	$a^3F_2 - z^1G_4^\circ$		
6,399.04	400	V ? E	623.04	$z^3G_4^\circ - e^3F_3$	(0.00) 1.04	(0.00) 1.06
90.48	200	III	643.96	$a^3D_2 - y^3F_3^\circ$	(0.00) 1.03	(0.00) 1.04
74.08	30	V	684.21	$z^3D_3^\circ - e^3D_2$	(0.00 w) 1.67 A^2	(0.00) 1.75 A^2
58.12	30	IV	723.58	$a^3P_1 - z^3D_1^\circ$	(0.99) 0.49, 1.52	(0.96) 0.54, 1.51
37.88	3	V	773.79	$a^3F_2 - z^1F_3^\circ$		
20.39	200	III	817.44	$a^1D_2 - y^3F_2^\circ$	(0.44) 0.87 B	(0.41) 0.87
15.79	50	V	828.96	$z^3P_1^\circ - e^3D_1$	(0.95) 0.49, 1.43	(0.96) 0.50, 1.46
10.91	200	V E	841.20	$z^3G_4^\circ - e^3G_4$	(0.27) 1.10 B	(0.29) 1.10
07.25	20 h	IV	850.40	$z^3P_0^\circ - e^3D_1$	(0.00) 0.51	(0.00) 0.50
6,305.46	10	IV	854.90	$a^3F_4 - z^3H_4^\circ$		
6,296.08	300	IV E	878.52	$b^1D_2 - y^3D_1^\circ$ $a^3P_2 - z^3D_2^\circ$	(0.00 w) 1.20 A^2	(0.00) 1.23 A^2
73.76	100	III ?	935.01	$y^1F_3^\circ - e^1D_2$	(0.00) 1.04	(0.00) 1.02
62.30	300	III	15,964.17	$a^3D_3 - y^3F_4^\circ$	(0.00 w) 1.10 A^1	(0.00) 0.96 A^1
6,203.51	50 l	V	16,115.46	$z^3D_3^\circ - e^3D_2$	(0.17) 1.14 h	(0.15) 1.14
6,188.09	100 l	V	155.61	$z^3P_2^\circ - e^3D_3$	(0.00 w) 1.02 A^1	(0.00) 0.99 A^1
74.15	6	V	192.09	$a^3P_0 - z^3D_1^\circ$	(0.00) 0.63	(0.00) 0.55
72.72	10	V	195.84	$a^3F_3 - y^3F_2^\circ$	(0.00, 0.32, 0.63) 1.69 A^2	(0.00, 0.34, 0.67) 1.76 A^2
46.53	15	IV	264.85	$a^3F_4 - y^3F_3^\circ$	(0.00 w) 1.69 A^2	(0.00) 1.76 A^2
1.92	1		303.60	$a^3D_2 - z^1D_2^\circ$		
29.57	50	IV ?	309.85	$a^3P_2 - z^3D_3^\circ$	(0.00 w) 0.99 A^1	(0.00) 0.98 A^1
26.09	50	V ?	319.12	$b^1D_2 - x^3F_3^\circ$	(0.34) 0.92 B	(0.32) 0.93
20.34	1	IV	334.45	$x^1P_1^\circ - i^1D_2$		
6,100.37	30	V	387.92	$a^3P_1 - z^3D_2^\circ$	(0.00, 0.34) 0.84, 1.16	(0.00, 0.32) 0.86, 1.19, 1.51
6,085.43	10	V	428.15	$z^3D_3^\circ - e^3D_1$	(0.00, 0.74) 1.20, 1.90	(0.00, 0.69) 0.50, 1.19, 1.88
74.01		III A	459.04	$z^3G_4^\circ - e^3F_4$	(0.21) 1.12	(0.27) 1.10

TABLE 4.—*The first spark spectrum of lanthanum (La II)*—Continued

λ_{air} I. A.	Intensity spark	Temperature class	ν_{vac} cm^{-1}	Term combinations	Zeeman effects	
					Observed	Computed
67.13	6	V ?	477.71	$a^3P_2-z^3P_1^\circ$	(0.00) 1.49	(0.00) 1.50
61.42	2	V ?	493.23			
46.07	2	IV ?	535.10			
6,037.98	2		557.25	$z^1D_2^\circ-e^3G_3$		
5,991.98	4 h		684.36	$z^3D_3^\circ-e^1G_4$		
73.52	120 l	V E	735.92	$z^3G_3^\circ-e^3G_3$	(0.00) 1.20	(0.00) 1.20
71.09	8		742.73	$b^1D_2-x^3F_3^\circ$	(0.00) 1.18	(0.00) 1.15
61.43	3		769.86	$z^3G_3^\circ-e^3G_4$		
57.90	4		779.80	$z^3D_1^\circ-e^3D_2$		
48.30	20		806.9	$z^3G_3^\circ-e^1F_3$	(0.52) 0.86 h	(0.46) 0.86
36.22	20	V E	841.08	$a^1D_2-y^3F_3^\circ$	(0.00) 1.21	(0.00) 1.19
27.71	30		865.26	$z^3D_3^\circ-e^3D_3$	(0.00) 1.30	(0.03) 1.31
18.26	4		892.19	$z^1D_2^\circ-e^3F_3$		
5,901.95	401	IV E	938.87	$z^3G_3^\circ-e^1G_4$	(0.00 w) 1.60 A[3]	(0.00) 1.78 A[3]
5,892.66	4	V	965.58	$a^3P_1-z^3P_0^\circ$	(0.00) 1.54	(0.00) 1.51
85.23	1		16,986.99	$a^3P_1-z^3P_1^\circ$		
80.63	50	III E ?	17,000.28	$a^3D_1-z^1D_2^\circ$	(0.00, 0.42) 0.54, 0.96, 1.38	(0.00, 0.41) 0.52, 0.93, 1.34
74.00	6	IV	019.47	$a^3P_2-z^3P_2^\circ$	(0.00) 1.49	(0.05) 1.48
63.70	80	V E	049.36	$a^1G_4-y^1F_3^\circ$	(0.00) 0.96	(0.00) 0.96
48.95	20		092.36	$z^3D_1^\circ-e^3D_1$	(0.00) 0.54	(0.05) 0.52
28.44	2		152.51	$a^3D_3-z^3G_3^\circ$		
08.63	8		211.00	$z^3P_2^\circ-e^1D_2$		
08.31	60	IV ?	211.95	$a^3F_2-y^3F_2^\circ$	(0.00) 0.75	(0.05) 0.74
06.56	8		217.14	$y^3F_3^\circ-e^3G_3$		
5,805.77	120	III E	219.48	$a^3F_3-y^3F_3^\circ$	(0.00) 1.09	(0.00) 1.09
5,797.57	150	III E	243.84	$a^3F_4-y^3F_4^\circ$	(0.00) 1.24	(0.05) 1.25
81.02	3		293.20	$b^1D_2-y^3D_3^\circ$		
79.91	4		296.52	$z^3D_2^\circ-e^3D_3$	(0.00) 1.38 h	(0.00) 1.43
69.06	60	V E	329.05	$b^1D_2-z^1P_1^\circ$	(0.00) 1.09	(0.00) 1.08
49.59	2		387.73	$z^3G_3^\circ-e^3F_4$		
27.29	20	V E	455.43	$a^3P_0-z^3P_1^\circ$	(0.00) 1.45	(0.00) 1.46
12.39	20	III E ?	500.96	$a^1D_2-z^1D_2^\circ$	(0.00) 0.98	(0.10) 0.96
5,703.32	20	III	528.80	$a^3P_1-z^3P_2^\circ$	(0.00) 1.48	(0.00) 1.44
5,671.54	100	V E	627.02	$z^3H_4^\circ-e^3G_3$	(0.00) 0.79	(0.00) 0.85
52.3	10 h		687.0	$z^3G_4^\circ-e^3G_3$		
5,610.53	20		818.69	$z^3G_3^\circ-e^1D_2$		
5,591.51	1		879.30	$a^3F_2-z^1D_2^\circ$		
66.92	40	V E	17,958.28	$y^3F_4^\circ-e^3G_4$	(0.37) 1.24	(0.32) 1.20
47.56	3 h		18,020.95		(0.00) 1.13	
35.66	80	V E	059.69	$b^1D_2-y^3P_1^\circ$	(0.00 w) 0.80 A[1]	(0.00) 0.77 A[1]
5,532.17	10	III	071.08	$z^3G_4^\circ-e^3D_3$	(0.00 w) 0.61 h	(0.00) 0.69
5,493.45	20	V E	198.45	$a^3F_3-y^3F_3^\circ$	(0.00 w) 1.57 A[3]	(0.00) 1.70 A[3]
86.86	5	V	220.31	$b^1D_2-y^3D_2^\circ$		
82.27	40	V E	235.57	$a^3F_2-y^3F_2^\circ$	(0.00 w) 1.89 A[3]	(0.00) 1.81 A[3]
80.72	25	V E	240.72	$y^3F_2^\circ-e^3G_3$	(0.00) 1.03 h	(0.00) 0.99
64.37	25	V E	295.30	$a^3P_2-y^1F_3^\circ$	(0.00, 0.49, 0.97) 0.00 d, 0.49, 0.97	(0.00, 0.46, 0.91) 0.12, 0.57, 1.03
58.68	50	V E	314.37	$z^1D_2^\circ-e^1F_3$	(0.00) 1.00	(0.00) 0.98
47.59	10		351.65	$z^3D_2^\circ-e^1D_2$	(0.22) 1.14	(0.25) 1.12
5,423.82	4		432.08	$a^3F_4-z^3G_4^\circ$		
5,381.91	100	V E	575.61	$y^3F_3^\circ-e^3F_2$	(0.00) 0.74	(0.00) 0.72
81.77	50	V E	576.10	$z^3F_4^\circ-e^3F_4$		
80.97	100	V E	578.86	$a^1S_0-y^1D_1^\circ$	(0.00) 0.77	(0.00) 0.80
77.08	200	V E	592.30	$z^3H_5^\circ-e^3G_4$	(0.00 w) 0.82 A[1]	(0.00) 0.83 A[1]
40.66	100	III E	719.09	$y^3F_3^\circ-e^3F_3$	(0.00) 1.07	(0.08) 1.08
33.42	2		744.50	$a^3P_1-y^1D_2$		
03.54	100	III E	850.10	$a^3D_2-z^3D_1^\circ$	(0.00, 0.61) 0.57, 1.17, 1.78	(0.00, 0.59) 0.55, 1.14, 1.73
02.62	150	V E	853.37	$z^1G_4^\circ-e^1G_2$	(0.00) 1.16	(0.00) 1.18
5,301.97	200	III E	855.68	$a^3D_3-z^3D_3^\circ$	(0.00 w) 1.50 w	(0.00) 1.49
5,290.83	50	III E	895.38	$a^3F_2-z^1D_2^\circ$	(0.34) 0.82 B	(0.36) 0.83
79.11	40	V E	18,937.33	$y^3F_3-e^3G_4$	(0.00) 1.20	(0.00) 1.23
59.38	50	III E	19,008.37	$a^1D_2-z^3G_3^\circ$	(0.00 w) 0.46 A[1]	(0.00) 0.35 A[1]
57.28	2		015.96	$z^3D_1^\circ-e^1D_2$		
26.20	40 l	V E	129.05	$z^3H_4^\circ-e^3F_3$	(0.00 w) 0.32 w	(0.00) 0.28 A[1]
22.48	3 h		142.68	$e^3D_2-1_3^\circ$	(0.00) 1.15	
21.32	3 h		146.93			

TABLE 4.—*The first spark spectrum of lanthanum (La II)*—Continued

λ_{air} I. A.	Intensity spark	Temperature class	ν_{vac} cm^{-1}	Term combinations	Zeeman effects	
					Observed	Computed
17.83	10 h		159.74			
5,204.14	300	V E	210.14	$z^3H_4^3-e^3F_4$	(0.00) 0.86 A[1]?	(0.00) 0.85 A[1]
5,191.50	3 h		256.91		(0.00) 1.05	
88.21	500	V E	269.12	$z^3H_4^4-e^3G_5$	(0.00) 1.09	(0.00) 1.09
83.42	400	III E	286.93	$a^3D_3-z^3D_3^3$	(0.00) 1.31	(0.05) 1.33
73.83	25 l	IV ? E	322.67	$x^1F_3^3-f^1D_2$	(0.00) 1.06	(0.00) 0.99
72.89	20 l	V E	326.19	$z^3D_3^3-e^3D_2$	(0.20 1.03	(0.30) 1.02
67.28	10		347.17	$z^3H_4-e^3G_4$		
63.61	40	V ? E	360.92	$a^3F_4-z^3G_4^3$	(0.74) 1.18 B	(0.66) 1.16
62.68	3		364.41	$a^1G_4-z^3F_3^3$		
57.43	150	V E	384.12	$z^3H_4^3-e^1F_3$	(0.00) 0.66	(0.00) 0.73
56.74	40	V E	386.71	$a^3F_3-z^3G_3^3$		
52.31	1		403.38	$b^1D_2-y^3P_2^3$		
22.99	200	III E	514.43	$a^3D_2-z^3D_2^3$	(0.00) 1.16	(0.08) 1.16
14.55	200	III ? E	546.63	$a^3D_1-z^3D_1^3$	(0.00) 0.54	(0.03) 0.53
12.37	2		554.97	$y^3F_3^3-e^3F_4$		
5,107.54	6 h		573.46	$e^3F_4-1_3^3$	(0.00) 1.19	
5,090.56	20 l	V E	638.74	$z^1D_2^3-e^3D_1$	(0.00 w) 1.33 A[2]	(0.00) 1.37 A[2]
86.71	3 hl		653.61	$x^3P_2^3-f^3G_3$		
80.21	40	V E	678.76	$z^1F_3^3-e^3G_3$	(0.38) 0.98 w	(0.45) 0.96
66.99	20 h		730.10	$e^3G_3-2_4^3$	(0.00) 1.10 h	
63.76	3		742.68	$y^3F_2^3-e^3F_3$		
62.91	20	V E	746.00	$a^3P_2-y^3D_1^3$	(**0.00**, 0.66) 0.90, 1.56, **2.22**	(**0.00**, 0.69) 0.80, 1.49, **2.18**
60.85	3		754.04	$z^3F_4^3-e^3G_3$		
58.56	1 h		762.97			
48.04	30 l	V E	804.16	$y^3F_4^3-3^3G_4$	(0.00) 1.16	(0.00) 1.12
14.45	30 hl		936.82	$x^1F_3^3-f^1F_3$		
5,002.12	40	V E	985.96	$y^3F_3^3-e^3D_2$	(0.00) 1.09	(0.00) 1.08
4,999.46	200	III E	19,996.60	$a^3D_3-z^3P_2^3$	(0.00 w) 1.28 A[2]	(0.00) 1.08 A[1]
96.82	50	V E	20,007.16	$y^3F_4^3-e^1G_4$		
95.17	1		013.77	$x^1F_3^3-e^3F_2$		
91.27	80	IV E	029.41	$a^1S_0-z^1P_1^3$	(0.00) 0.85	(0.00) 0.88
86.82	100	III E	047.28	$a^1D_2-z^3D_1^3$	(**0.00**, 0.43) 0.57, 1.00, **1.43**	(**0.00**, 0.44) 0.55, 0.99, **1.43**
74.20	4 h		098.14	$x^3P_2^3-e^1P_1$		
70.39	100	III E	113.55	$a^3D_3-z^3P_2^3$	(**0.00**, 0.29) **0.83**, 1.12 us	(**0.00**, 0.32) **0.82**, 1.14, **1.46**
56.04	2	V	171.79			
52.06	40	V E	188.00	$y^3F_4^3-e^3D_3$	(0.00) 1.17.	(0.00) 1.15
46.47	50	IV?E	210.81	$a^3D_1-z^3D_2^3$	(**0.00**, 0.67) 1.15, **1.82**	(**0.00**, 0.67) 0.52, 1.19, **1.85**
35.61	10	V E	255.28	$a^3P_1-y^3D_1^3$		
34.83	100	V E	258.48	$b^1D_2-y^1P_1^3$	(0.00) 0.97	(0.00) 0.99
21.80	300	III E	312.12	$a^3F_4-z^3G_4^3$	(0.00) 1.11	(0.00) 1.09
20.98	300	III E	315.50	$a^3F_3-z^3G_3^3$	(0.00) 1.00	(0.00) 0.92
11.34	10		355.38	$z^1G_4^3-e^3F_3$		
4,904.43	2 h		384.05	$x^3P_0^3-y^3D_1$		
4,899.92	200	III E	402.82	$a^3F_2-z^3G_3^3$	(0.00) 0.80	(0.00) 0.82
91.43	10		438.23	$z^3H_5-e^3G_5$		
80.20	10 h		485.17	$x^3P_2^3-y^3D_2$		
74.99	1		507.15	$z^1D_2-e^3D_2$		
60.90	80	III E	566.59	$a^3F_4-z^3D_3^3$	(0.00) 1.19	(0.00) 1.17
59.18	5 h		573.87	$z^1G_4^3-e^3G_4$		
				$z^3P_1^3-z^3D_2$		
50.58	30	V E	610.35	$a^3P_2-x^3F_3^3$		
				$z^1G_4-e^1F_3$	(0.00) 1.03	(0.00) 1.06
43.29	5	V	641.37			
40.02	30	V E	655.32	$a^3D_2-z^3P_2^3$	(0.67) 1.30 ?	(0.58) 1.30
30.51	10	V E	695.98	$a^3P_1-z^3F_2^3$	(0.00) 0.76 R	(**0.00**, 0.67) **0.17**, 0.84 1.51
26.87	20	V E	711.59	$a^1D_2-z^3D_2^3$	(0.33) 1.08 R	(0.36) 1.09
24.05	100	III E	723.70	$a^3P_0-y^3D_1^3$	(0.00) 0.79	(0.00) 0.80
09.00	100	V E	788.55	$a^3D_1-z_3P_2^3$	(0.00) 0.51	(0.00) 0.52
4,804.04	80	V E	810.02	$a_3D_1-z_3P_1^3$	(0.95) 0.49, **1.43**	(0.94) 0.52, 1.46
4,796.67	25	V E	841.99	$a^1G_4-y_3D_3^3$		
94.55	3	V E	851.20			

TABLE 4.—*The first spark spectrum of lanthanum (La II)*—Continued

λ_{air} I. A.	Intensity spark	Temperature class	ν_{vac} cm^{-1}	Term combinations	Zeeman effects	
					Observed	Computed
80.55	2	V	20,912.27			
58.40	3		21,009.61	$y^3F_2^3$—e^3D_2		
48.73	150	V E	052.39	a^1G_4—$z^1H_5^6$	(0.00) 1.00	(0.00) 0.99
43.08	250	V E	077.47	$z^3F_3^4$—e^3G_3	(0.52 w) 0.95 B	(0.55) 0.98
40.27	120	III E	089.96	a^3F_3—$z^3D_3^4$	(0.00 w) 0.97 A_{-1}	(0.00) 0.90 A 1
39.80	15	V E	092.06	a^1G_4—x^3F_4		
30.73	3 h		132.50	$x^1F_3^4$—f^1G_4		
28.41	100	V E	142.86	a^1D_2—$z^3D_3^4$	(0, 00, 0.32) 1.31, 1.61, 1.91	0.00, 0.33, 0.66)—, —, 1.32, 1.65, 1.99
24.42	40	V E	160.72	a^3P_2—$y^3D_3^4$	(0.65) 0.95 us	(0.30, 0.59) 0.89, 1.19, 1.49, 1.78
22.14	2 h		170.94	$y^1P_1^4$—f^1D_2		
19.93	150	V E	180.85	$z^1F_3^4$—e^3F_3	(0.00) 1.06	(0.00) 1.05
17.58	50	V E	191.40	$z^1G_4^4$—e^3F_4	(0.50) 1.2	(0.48) 1.07
16.44	80	V E	196.52	a^3P_2—$z^1P_1^4$	(0, 00, 0.60) 0.92, 1.52, 2.12	(0, 00, 0.61) 0.88, 1.49 2.09
12.92	40	V E	212.35	a^3D_3—$y^1D_2^4$	(0, 00, 0.47, 0.92) 1.83, 2.26 R	(0, 00, 0.44, 0.88) —, —, —, 1.78, 2.22
4,703.27	150	V E	255.87	$z^3F_4^4$—e^3F_3	(0.00 w) 1.70 A^3	(0.00) 1.85 A^3
4,699.62	50	V E	272.38	a^3D_3—$y^1F_3^4$		
92.50	200	V E	304.66	$z^3F_3^4$—e^3G_3	(0.00 w) 1.21 A^3	(0.00) 1.26 A^3
91.17	50	V E	310.70	a^1D_2—$z^3P_1^4$	(0.00, 0.46) 0.46 us	(0, 00, 0.47) 0.51, 0.99, 1.46
88.65	40	V E	322.15	$y^3F_2^3$—e^3D_1	(0.00) 0.96	(0.00) 0.89
84.39	2 h		341.54	e^3D_3—4_3^4		
82.12	5		351.89	a^3D_1—$^{23}P_2^3$		
73.53	1 h		391.14	e^3D_3—$3_{3,2}^4$		
71.82	200	V E	398.96	$z^1F_3^4$—e^3G_4	(0.00 w) 1.29 h	(0.00) 1.30
68.91	250	V E	412.30	$z^3F_3^4$—e^3F_2	(0, 00, 0.34, 0.68) 0.77, 1.12 1.47, 1.81 us	(0, 00, 0.36, 0.71) —, —, 0.73, 1.09, 1.44, 1.80
63.76	300	V E	435.94	$z^1F_3^4$—e^1F_3	(0.20) 0.99	(0.24) 0.99
62.51	200	III E	441.69	a^3F_2—$z^3D_1^4$	(0.00 w) 0.89 A^2	(0.00) 0.91 A^3
55.49	400	V E	474.02	$z^3F_4^4$—e^3G_4	(0.43) 1.20 B	(0.37) 1.20
52.07	30 hl	I	489.81			
47.50	100	V E	510.94	$z^3F_4^4$—e^1F_3	(0, 00, 0.31, 0.61) 1.98 A^3	(0, 00, 0.30, 0.61) 2.17 A^3,
45.28	100	V E	521.22	a^3F_3—$z^3D_3^4$	(0.60) 1.26 B	(0.58) 1.20
41.40	2 h		539.21	e^1F_3—2_2^4		
36.42	80	V E	562.35	$z^1D_2^4$—e^1D_2	(0.21) 1.00	(0.21) 0.99
34.95	25 l		569.19	$y^3D_1^4$—f^1D_2	(0.00) 1.43	(0.00) 1.48
23.99	2 h		620.31			
19.87	300	V E	639.59	$z^3F_3^4$—e^3F_2	(0.00) 0.70	(0.10) 0.70
13.38	200	V E	670.03	a^3P_1—$y^3D_2^4$	(0, 00, 0.33) 0.83, 1.16, 1.49	(0, 00, 0.32) 0.88, 1.19, 1.51
05.78	100	V E	705.79	a^3P_1—$z^1P_1^4$	(0.63) 0.89, 1.52	(0.62) 0.88, 1.51
01.65	3		725.27	e^3G_3—4_3^4		
4,600.59	5 h		730.27	$y^3F_2^3$—f^1D_2 $y^3P_1^4$—f^3D_2		
4,595.06	2 h		756.42			
87.14	2 h		793.99	e^3F_2—2_2^4		
80.05	150	V E	827.73	a^3P_1—$y^3P_2^3$	(0.00) 1.51	(0.00) 1.51
74.87	200	III E	852.44	a^1D_2—$z^3P_2^3$	(0.49, 0.98) 0.49, 0.98, 1.46, 1.94	(0.48, 0.95) 0.51, 0.99 1.46, 1.94
70.97	10	V E	871.08	a^3D_2—y^1D_2	(0.43) 1.00 R	(0.44) 1.02
62.5	5 h		911.7	e^3G_3—1_3^4		
59.28	100	V E	927.16	a^3P_2—$y^3P_1^4$	(0.00, 0.18) 1.62	(0.00, 0.23) 1.26, 1.46, 1.71
58.46	200	III E	21,931.10	a^3D_3—$y^1F_3^4$	(0.00 w) 0.88 A^1	(0.00) 0.82 A^1
40.71	10		22,016.84	$z^1F_3^4$—e^3F_4	(0.00) 1.27	(0.00) 1.28
38.87	8 hl		025.76	$y^3P_2^3$—f^1D_2		
30.54	15	V E	066.26	b^1D_2—$x^3P_1^4$		
26.12	200	III E	087.81	a^3P_2—$y^3D_3^4$	(0.00 w) 1.01 A^1	(0.00) 0.96 A^1
25.31	100	V E	091.76	$z^3F_4^4$—e^3F_4	(0.46) 1.19 B	(0.39) 1.20
22.37	400	III E	106.12	b^1D_2—$x^1F_3^4$ a^3F_2—$z^3D_2^4$	(0.00) 1.02	(0.00) 1.00
16.38	5 hl		135.44			
08.48	10		174.22	a^3P_0—$z^1P_1^4$	(0.00) 0.90	(0.00) 0.88

TABLE 4.—*The first spark spectrum of lanthanum (La II)*—Continued

λ_{air} I. A.	Intensity spark	Temperature class	ν_{vac} cm^{-1}	Term combinations	Zeeman effects	
					Observed	Computed
05.82	3 hl		187.32	$y^3P^0_2$—f^3D_1		
4,502.16	10 hl		205.35	$x^3P^0_1$—e^3S_1	(0.00) 1.47	(0.00) 1.47
4,498.76	10		222.13	$y^3F^0_3$—e^1D_2	(0.00) 1.14	(0.00) 1.13
97.00	2		230.83	a^3F_2—$z^3F^0_2$		
84.48	1 h		292.90	e^1G_4—$6i_{4,3}$		
81.21	25 hl		309.16	$z^1P^0_1$—f^3D_1	(0.40) **0.50**, 0.87	(0.36) 0.52, 0.88
74.03	10		344.96	$y^1D^0_2$—f^3D_1	(**0.00**, 0.66) 0.50, 1.17, **1.83**	(**0.00**, 0.67) 0.52, 1.19, **1.86**
59.10	3		419.78	$z^1G^0_4$—e^3G_5		
55.79	50	V E	436.43	a^3P_1—$y^3P^0_1$	(0.24) 1.41	(0.24) 1.38
43.94	20 hl	I	496.26	$y^3D^0_2$—f^3D_2	(0.00) 1.18 h	(0.09) 1.17
35.84	10	IV E	537.34	$a^3F^0_2$—$z^3D^0_2$	(**0.00**, 0.60, 1.19) 1.28, **1.86**, **2.44**	(**0.00**, 0.59, 1.17) —, —, 1.32, 1.90, **2.49**
32.95	20?		552.03	a^3F_4—$y^1F^0_3$		
29.90	400	III E	567.56	a^3D_1—$y^1D^0_2$	(**0.00**, 0.40) 0.51, 0.91, **1.31**	(**0.00**, 0.38) 0.52, 0.90, **1.27**
27.52	100	V E	579.69	$z^3F^0_3$—e^3F_3	(0.00 w) 1.06	(0.07) 1.07
19.16	30	V E	622.41	$z^1G^0_4$—e^1G_4	(0.28) 1.04	(0.21) 1.03
17.14	2 h	III	632.75	$x^3P^0_1$—e^1S_0		
12.22	2 h		657.98	e^3F_3—$3i_{3,2}$		
11.21	25 hl	V E	663.17	$x^3F^0_4$—f^3D_3	(0.00 h) 1.13 h	(0.00) 1.12
4,403.02	2	III A	705.33	a^3F_3—$z^3P^0_2$		
4,385.20	40	V E	797.59	$z^3F^0_{3,2}$—e^3G_4	(0.00) 1.24	(0.00) 1.24
83.44	100	V E	806.75	$z^3F^0_3$—e^3F_3	(**0.00**, 0.40, 0.80) 0.28, 0.68, 1.08, 1.48, **1.88**	(**0.00**, 0.38, 0.77) 0.29, 0.68, 1.06, 1.45, **1.83**
78.10	50	IV E	834.56	$z^3F^0_4$—e^1F_3	(0.30 w) 0.95	(0.34) 1.02
64.66	100	IV E	904.88	a^3P_0—$y^3P^0_1$	(0.00) 1.28	(0.00) 1.26
63.05	50 l	V E	913.33	$y^3D^0_3$—f^3D_3	(0.00 h) 1.32 h	(0.03) 1.32
56.18	1		949.46	$y^1P^0_1$—e^1P_1		
54.40	200	IV E	22,958.84	a^1S_0—$y^1P^0_1$	(0.00) 1.08	(0.00) 1.07
37.78	10 l		23,046.81	$x^3F^0_3$—f^3D_2	(0.00) 1.08 h	(0.00) 1.02
34.96	100	V E	061.80	$z^3F^0_2$—e^1F_3	(**0.00**, 0.29, 0.57) 0.69, 0.97, 1.26, **1.54**	(**0.00**, 0.28, 0.55) −0.68, 0.95, 1.23, **1.51**
33.76	500	III E	068.19	a^1D_2—$y^1D^0_2$	(0.17) 0.94	(0.16) 0.94
22.51	100	III E	128.22	a^1D_2—$y^1F^0_3$	(0.00) 1.10	(0.00) 1.08
15.90	30	V E	163.65	a^3D_3—$z^3F^0_4$	(**0.00**, 0.50, 1.00) 0.86, 1.36, 1.86, **2.36**	(**0.00**, 0.50, 1.00) −0.84, 1.34, 1.84, **2.34**
04.11	10 hl		227.10	e^3F_4—$5i_{4,3}$	(0.00 h) 1.24 h	
4,300.44	60	IV E	246.92	a^3F_2—$z^3P^0_2$	(0.73, **1.48**) 0.00, **0.72**, **1.45**, 2.18	(0.73, **1.46**) 0.00, **0.73**, **1.46**, 2.19
4,296.05	300	IV E	270.67	a^3P_2—$y^3P^0_2$	(0.00) 1.48	(0.02) 1.49
86.97	300	V E	319.96	$z^3F^0_4$—e^1G_4	(0.00) 1.08	(0.00) 1.09
75.64	100	IV E	381.75	a^3D_3—$y^3D^0_1$	(**0.00**, 0.35) 0.82, 1.17, **1.52**	(**0.00**, 0.34) 0.80, 1.14, **1.48**
69.50	300	V E	415.38	$z^3F^0_3$—e^3F_4	(0.00) 1.20	(0.00) 1.22
63.59	200	V E	447.83	$z^1F^0_3$—e^1G_4	(0.00) 1.12	(0.00) 1.08
59.51	2 h		470.30	$x^3F^0_2$—f^3D_2		
56.50	3		486.89			
52.93	4		506.61	a^3F_3—$y^1F^0_3$		
49.99	100	V E	522.87	$z^3F^0_4$—e^1G_4	(0.74) 0.50, 0.76, **1.02**, **1.27**, 1.53, 1.76	(—, —, 0.59, **0.79**) 0.50, 0.75, **1.00**, **1.25**, 1.50, 1.75
48.32	2		532.11	$y^1P^0_1$—f^3F_2		
41.20	15 hl		571.62	e^3G_4—$4i^0_4$		
38.38	400	III E	587.30	a^3D_3—$z^3F^0_4$	(0.74) 0.56, 0.82, **1.08**, **1.34**, 1.60, 1.86	(—, 0.51, **0.77**) 0.57, 0.83, **1.08**, **1.34**, 1.59, 1.85
30.95	150	V E	628.72	$z^1F^0_3$—e^3D_3	(0.80) 0.65, 0.85, **1.06**, **1.26**, 1.47, 1.67 ur	(—, 0.52, **0.78**) 0.53, 0.79, **1.05**, **1.31**, 1.56, 1.82
17.56	200	V E	703.74	$z^3F^0_4$—e^3D_3	(0.00) 1.22	(0.00) 1.19
10.22	50 hl		745.06		(0.00 h) 1.02 h	
07.61	10 l		759.79	$y^3D^0_1$—f^3D_1	(0.27) 0.68 h	(0.28) 0.66
04.03	100	V E	780.02	a^3P_1—$y^3P^0_2$	(0.00) 1.48	(0.00) 1.49
4,201.50	6 h		794.34			
4,196.55	250	III E	822.41	a^3D_3—$z^3F^0_3$	(0.32, **0.64**) 0.51, **0.82**, **1.13**, 1.44	(0.30, **0.61**) 0.53, **0.84**, **1.14**, 1.44
94.36	30 h		834.85	$x^1F^0_3$—f^1G_4	(0.00 h) 1.06 h	(0.00) 1.06
93.34	5		840.64	[$y^3D^0_3$—f^3D_3]	(0.25) 0.64	(0.00) 1.47 (?)
92.35	100	V E	846.27	$z^3F^0_2$—e^3D_2	(0.00) 1.06	(0.00) 1.07

TABLE 4.—*The first spark spectrum of lanthanum (La II)*—Continued

λ_{air} I. A.	Intensity spark	Temperature class	ν_{vac} cm^{-1}	Term combinations	Zeeman effects	
					Observed	Computed
80.97	12 l		23,911.18	$y^3D_1^\circ$—f^3D_2		
61.94	8 h		24,020.51		(0.00 h) 1.02	
54.59	2 h		063.00	e^3F_3—$5f_{3,2}$		
52.78	100	IV ? E	073.49	$z^3F_2^\circ$—e^3D_2	(0.43, 0.84) 0.27, 0.67, 1.08, 1.48	(0.42, 0.85) 0.25, 0.68, 1.10, 1.52
51.98	250	III E	078.13	a^3D_1—$y^3D_1^\circ$	(0.29) 0.50, 0.77	(0.28) 0.52, 0.80
48.2	4 h		100.1	$z^1P_1^\circ$—f^1D_2		
43.77	15		125.83	a^3P_2—$y^1P_1^\circ$		
41.73	200	IV E	137.72	a^3D_2—$y^3D_2^\circ$	(0.00 w) 1.50 w	(0.00) 1.48
37.91	2		160.00	e^3G_3—$3f_{3,2}$		
33.33	6 hl		186.77		(0.00) 0.97	
32.50	10 hl		191.63	$y^3P_2^\circ$—g_3D_3	(0.00 h) 0.83 h	(0.00) 0.92
31.74	5 h		196.08	e^3D_3—$7f_{4,3}$	(0.00 h) 1.13 h	
23.23	400	III E	246.01	a^3D_2—$z^3F_3^\circ$	(0.00) 1.05	(0.00) 1.02
15.35	1 h		292.44	$x^3F_4^\circ$—f^3G_3		
13.28	40 l		304.66	e^1F_3—$6f_{4,3}$	(0.00 h) 1.09 h	
4,101.01	3 h		377.38	e^1G_4—$7f_{4,3}$		
4,099.54	150	V E	386.12	$z_3F_2^\circ$—e^3D_1	(0.00) 0.77	(0.00) 0.77
98.73	5		390.94	$x^3F_3^\circ$—f^3D_3		
86.72	300	III E	462.62	a^3F_2—$y^1D_2^\circ$	(0.32) 0.79 w	(0.30) 0.81
77.35	300	III E	518.84	a^3D_1—$z^3F_2^\circ$	(0.00, 0.32) 0.57, 0.89, 1.20	(0.00, 0.32) 0.52, 0.84, 1.15
76.71	40	IV E	522.68	a^3F_2—$y^1F_3^\circ$	(0.00, 0.31, 0.62) 0.79, 1.08, 1.38, 1.69	(0.00, 0.30, 0.60) —, 0.73, 1.03, 1.33, 1.64
67.39	100	IV E	578.88	a^1D_2—$y^3D_1^\circ$	(0.00 w) 1.14 A^3	(0.00) 1.17 A^3
58.08	5 t		635.26	a^3P_1—$y^1P_1^\circ$	(0.45) 1.06, 1.47 us	(0.44) 1.07, 1.51
50.08	200	V E	683.92	$z^1F_3^\circ$—e^1D_2	(0.00) 1.02	(0.00) 1.05
42.91	300	IV E	727.70	a^1G_4—$x^1F_3^\circ$	(0.00) 0.99	(0.00) 1.00
36.59	15 d	V E	766.41	a^1S_0—$x^3P_1^\circ$	(0.00) 1.54	(0.00) 1.52
31.68	300	III E	796.57	a^3D_3—$y^3D_3^\circ$	(0.00) 1.15	(0.09) 1.17
25.87	50	IV E	832.36	a^3D_2—$z^1P_1^\circ$	(0.00 w) 1.37 A^3	(0.00) 1.40 A^3
23.58	40	IV E	846.49	$y^3F_3^\circ$—e^1G_4	(0.00) 1.07	(0.00) 1.02
20.19	2 h		867.44	$y^3P_2^\circ$—e^3S_1		
4,007.64	7 h		24,945.32		(0.00 w) 1.01 h	
3,995.74	400	III E	25,019.61	a^1D_2—$x^3F_3^\circ$	(0.30) 0.90 w	(0.27) 0.91
94.50	10		027.37	$z^3F_3^\circ$—e^3D_3	(0.57 h) 1.25 h	(0.56) 1.20
88.51	500	III E	064.96	a^3D_3—$y^3D_3^\circ$	(0.00) 1.32	(0.06) 1.32
81.36	10 l		109.97	$x^3F_2^\circ$—f^1D_2	(0.38) 0.98 h. us	(0.33) 0.93
79.08	8 l		124.35	$x^3F_4^\circ$—g^1D_2	(0.00) 1.26	(0.00) 1.30
63.04	5 l		226.04		(0.00 w) 0.82 h	
62.03	10 l		232.47		(0.00) 1.10 h	
58.53	2		254.78	$z^3F_2^\circ$—e^3D_2		
57.25	2		262.95			
56.07	4		270.48	$y^1D_2^\circ$—f^3D_1	(0.00 h) 1.29 h	(0.00) 1.27
55.21	3 h		275.98		(0.00) 1.15	
53.36	2		287.81		(0.00) 1.06	
51.43	3 h		300.16	$x^3F_3^\circ$—f^1F_3		
49.10	600	III E	315.09	a^3D_2—$x^3F_3^\circ$	(0.00) 1.13 w	(0.00) 1.11
44.15	3		346.86	$y^3D_3^\circ$—g^3D_3	(0.00) 1.18 h	(0.04) 1.18
39.85	20 l		374.52	$y^3D_1^\circ$—g^3D_2	(0.21) 1.27 h	(0.26) 1.26
36.22	50	IV E	397.92	a^3F_3—$x^3F_3^\circ$	(0.00, 0.25, 0.48), 0.86, 1.10, 1.34, 1.58.	(0.00, 0.26, 0.51) —, —, 0.84, 1.09, 1.35, 1.60
32.53	10 l		421.75	$y^1D_2^\circ$—f^3D_2	(0.44) 1.06 B	(0.44) 1.02
30.47	3		435.07		(0.00) 0.92	
29.22	300	III E	443.17	a^1D_2—$x^3F_3^\circ$	(0.00) 1.20	(0.00) 1.18
25.09	5		469.94	$y^3D_3^\circ$—f^3O_3		
24.69	3		472.53		(0.00 h) 0.72 h	
21.54	200	III E	492.99	a^3D_1—$y^3D_2^\circ$	(0.00, 0.66) 0.52, 1.18, 1.84	(0.00, 0.67) 0.52, 1.19, 1.86
16.05	300	III E	528.73	a^3D_1—$z^1P_1^\circ$	(0.38) 0.51, 0.88	(0.36) 0.52, 0.88
3,910.81	10 l	IV ? E	562.94	a^3D_2—$y^3P_1^\circ$	(0.00) 1.04	(0.00) 1.08
3,897.43	4		650.70	a^3D_1—$y^3P_0^\circ$		
92.47	3		683.37	$y^1P_1^\circ$—e^3P_2	(0.00 h) 1.4 h	(0.00) 1.30
92.05	3		686.15	$y^3P_2^\circ$—g^1D_2		
86.37	150	III E	723.69	a^3D_2—$y^3D_2^\circ$	(0.00 w) 1.62 A	(0.00) 1.66A

TABLE 4.—*The first spark spectrum of lanthanum* (*La II*)—Continued

λ_{air} I. A.	Intensity spark	Temperature class	ν_{vac} cm^{-1}	Term combinations	Zeeman effects	
					Observed	Computed
85.09	4		732.16	$y^3P^0_2-e^3P_1$		
71.64	200	III ? E	821.56	$a^3F_3-x^3F^0_3$	(0.00) 1.08	(0.00) 1.09
68.35	3 h		843.52			
64.49	100 l		869.33	$x^3F^0_4-f^3G_5$	(0.00 h) 1.10 h	(0.00) 1.11
63.11	2		878.57	$z^1P^0_1-e^1P_1$		
60.31	2		897.34	$x^3F^0_3-g^3D_2$		
54.91	30		933.62	$a^3P_2-x^3P^0_1$	(0.00) 1.50	(0.00) 1.48
49.02	100	III ? E	973.30	$a^3F_2-y^3D^0_1$	(0.00) 0.69	(0.00) 0.70
46.00	20	V ? E	25,993.69	$a^1D_2-y^3D^0_2$	(0.36) 1.11 B	(0.37) 1.09
40.72	60	V ? E	26,029.43	$a^1D_2-z^1P^0_1$	(0.00) 1.04	(0.00) 1.04
36.4	1		058.7	$x^1F^0_3-g^3F_4$		
35.09	50	V E	067.64	$a^3P_1-x^3P^0_0$	(0.00) 1.49.	(0.00) 1.51.
17.24	8 h		189.53	$e^3D_2-8^0_3$	(0.00) 0.82 h.	
16.25	10 h		196.33	$y^3D^0_1-g^3D_1$	(0.00 h) 0.68.	(0.13) 0.73.
14.1	2		211.1	$y^3P^0_1-e^3S_1$		
08.79	15		247.63	$a^3D_3-y^3P^0_2$	(0.00 w) 1.18 h	(0.00) 1.18
07.1	1		259.3	$a^3D_1-y^3P^0_1$		
04.8	2 h		275.2	$x^3F^0_4-f^3F_3$		
3,801.0	1		301.4	$y^3D^0_2-g^3D_3$		
3,798.19	2		320.88	$x^3F^0_2-g^3D_2$		
94.78	400	III E	344.54	$a^3F_4-y^3D^0_3$	(0.00) 1.16	(0.00) 1.18.
90.83	300	III E	371.99	$a^3F_3-y^3D^0_2$	(0.00) 1.00.	(0.00) 0.99.
84.81	15	V E	413.93	$a^3F_2-x^3F^0_2$	(0.17) 0.79.	(0.19) 0.78.
83.06	1		426.15	$e^3G_4-7^0_{4,3}$		
80.67	50?	V E	442.85	$a^3P_1-x^3P^0_1$	(0.00) 1.54.	(0.01) 1.51.
80.53	50?		443.84	$x^3F^0_2-f^3G_3$	(0.00 h) 0.92 h.	(0.00) 0.94.
73.12	150 l		495.77	$x^3F^0_3-f^3G_4$	(0.00) 1.00 h.	(0.00) 1.00.
68.98	3 h		524.87	$y^3D^0_3-f^3F_3$		
67.05	5 h		538.46	$y^3P^0_2-e^3P_2$	(0.47) 1.24 B.	(0.50) 1.36.
66.58	3 h		541.77	$x^3F^0_4-e^3H_4$		
59.08	300	III E	594.72	$a^3F_4-x^3F^0_4$	(0.00) 1.25.	(0.04) 1.25.
53.04	2 h		637.52	$z^3P^0_2-f^3D_2$		
47.96	5 l		673.63		(0.00 w) 0.90 h.	
44.85	2 h		695.78			
36.41	15 l		756.08	$x^3F^0_4-f^3F_4$	(0.37) 1.20 B.	(0.29) 1.20.
35.85	10	IV E	760.09	$a^1D_2-y^3P^0_1$	(0.00 w) 0.90 d	(0.00) 0.85
35.09	1		765.53	$y^1D^0_2-f^3D_2$		
31.42	8 h		791.86	$y^3D^0_3-e^3H_4$		
28.97	2 h		809.46	$y^3P^0_1-e^3P_0$		
25.05	20	IV E	837.67	$a^3F_2-x^3F^0_3$	(0.00, 038, 0.75) 0.79, 1.16, 1.53, **1.90**	(0.00, 0.35, 0.70) −, 0.73, 1.08, 1.43, **1.78**
20.75	2		868.69	$y^3D^0_3-g^1D_2$		
17.99	2		888.63	$x^3F^0_2-e^1P_1$		
15.53	50	IV E	906.44	$a^3D_2-y^3P^0_2$	(0.40, **0.72**) 0.80, **1.13**, **1.46**, 1.79	(0.36, **0.71**) 0.78, **1.14**, **1.50**, 1.85
14.87	40	V E	911.22	$a^3P_0-x^3P^0_1$	(0.00) 1.50	(0.00) 1.52
13.54	100	IV E	920.85	$a^1D_2-y^3D^0_3$	(0.00, 0.34, 0.68) 1.00, 1.35, 1.69, **2.03**	(0.00, 0.32, 0.65) −, 0.99, 1.31, 1.64, **1.96**
10.61	2		942.11	$z^1P^0_1-e^3S_1$		
05.81	80	V E	26,977.01	$a^3P_2-x^3P^0_2$	(0.00) 1.51	(0.02) 1.48
3,701.81	40 l	V E	27,006.15	$y^3D^0_3-f^3F_4$	(0.00 w) 0.73 A[1]	(0.00) 0.70 A[1]
3,696.11	2 h		047.80	$x^3F^0_3-f^3F_2$		
95.2	2 h		054.5			
94.27	7 h		061.27	$y^1D^0_2-f^1D_2$	(0.36) 0.88 h	(0.22) 0.96
92.31	2 h		075.64	$y^3P^0_1-e^3P_1$		
78.24	2 h		179.20	$z^3P^0_1-f^3D_2$		
75.22	1		201.54	$e^1F^3-8^0_3$		
70.23	4 h		238.52	$e^3G^4-8^0_3$	(0.30) 1.06	
69.27	3 h		245.65			
65.22	10 l		275.75	$x^3F^0_2-g^3D_3$?	(0.00 d) 1.92 d	(0.00, 0.37, −) −, −, 1.51, **1.96**.
62.08	30	IV E	299.14	$a^3F_3-y^3D^0_2$	(0.66) 1.16 B	(0.57) 1.20
58.40	3		326.60	$x^1F^0_3-g^1G_4$	(0.00) 1.0	(0.00) 1.17
58.04	1		329.29	$y^3D^0_1-e^1P_1$		

TABLE 4.—*The first spark spectrum of lanthanum (La II)*—Continued

λ_{air} I. A.	Intensity spark	Temperature class	ν_{vac} cm^{-1}	Term combinations	Zeeman effects	
					Observed	Computed
56.62	1 h		369.84	$z^1P_1^\circ$—e^1S_0		
50.19	80	V E	388.06	a^3F_3—$y^3D_2^\circ$	(0.48, 0.91) 0.29, 0.73, 1.18, 1.62	(0.46, 0.92) 0.27, 0.71, 1.19, 1.65
45.43	200	IV E	423.82	a^3F_2—$z^1P_1^\circ$	(0.00) 0.66	(0.00) 0.65
41.66	50 l		452.21	$y^3D_3^\circ$—f^3F_3	(0.00) 1.21	(0.00) 1.09
41.10	2		456.43	$z^1H_5^\circ$—e^3H_5	(0.00) 1.01	(0.00) 1.02
39.25	3 h		470.39	$x^3F_4^\circ$—f^1G_4		
37.15	40	V E	486.25	a^3P_1—$x^3P_2^\circ$	(0.00) 1.51	(0.00) 1.46
29.99	2 hl		540.46	$z^1P_1^\circ$—e^3P_0		
28.83	60	IV E	549.27	a^3F_3—$x^3F_4^\circ$	(0.00 w) 1.68 A[3]	(0.00) 1.71 A[3]
21.77	4	V E	602.97	a^3D_1—$y^3P_2^\circ$		
20.16	1		615.24	$y^1F_3^\circ$—f^1F_3		
18.60	1		627.15	$z^3D_2^\circ$—f^3D_1		
12.34	50	V E	675.02	$y^1D_2^\circ$—f^1F_3	(0.00) 1.11	(0.00) 1.10
11.09	2		684.60	$y^3P_0^\circ$—e^3P_1	(0.00) 1.57 h	(0.00) 1.57
10.25	30 l		691.04		(0.00) 1.02	(0.00) 1.03
09.22	4		698.95	$x^1F_3^\circ$—h^1D_2	(0.00) 1.00	(0.00) 1.01
08.18	4		706.93	$y^1D_2^\circ$—g^3D_1	(0.00w) 1.08 A[3]	(0.00) 1.12 A[3]
06.42	4 hl		720.45	$y^3D_3^\circ$—f^1G_4		
3,601.07	20 hl	v E	761.63	a^3D_2—$y^1P_1^\circ$	(0.00) 1.18	(0.00) 1.17
3,598.93	3 hl		778.14	$z^3D_3^\circ$—f^3D_2	(0.00) 1.15	(0.08) 1.16
96.65	4 hl		795.75	$y^3D_2^\circ$—g^1D_2	(0.00) 1.22	(0.20) 1.14
93.29		v E	821.74			
92.42	2 h		828.48			
90.66	1 h		842.11	$y^3D_3^\circ$—e^3P_1		
85.53	2		881.95	$y^3P_1^\circ$—e^3P_2	(0.00) 1.25	(0.00) 1.20
81.68	20 hl		911.92	$y^3D_1^\circ$—f^3F_2	(0.00) 0.74	(0.00) 0.76
80.10	8 h		924.24	$x^3P_2^\circ$—f^3P_1	(0.00) 1.52	(0.00) 1.48
78.89	5 h		933.68	$x^3P_1^\circ$—f^3P_0	(0.00) 1.44	(0.00) 1.52
76.56	2 hl		27,951.88	$x^3F_2^\circ$—e^3S_1		
70.10	30 hl		28,002.38	$x^3F_3^\circ$—f^3F_3	(0.00) 1.08	(0.15) 1.11
57.26	8	IV ? E	103.53	a^1D_2—$y^3P_2^\circ$		
50.82	6	IV ? E	154.49	a^3F_2—$y^3P_1^\circ$		
36.37	3 h		269.53	$x^3F_4^\circ$—e^3H_4		
33.67	3 h		291.13	$z^3D_1^\circ$—f^3D_1		
30.67	8	V ? E	315.17	a^3F_2—$y^3D_3^\circ$		
26.77	2 h		346.48	$x^3F_3^\circ$—g^1D_2		
20.72	10 hl		395.19	$y^1D_2^\circ$—f^1G_4	(0.00) 0.88	(0.00) 0.88
14.87	2 h		442.45	$z^3D_1^\circ$—f^1D_2		
12.93	10	IV E	458.15	a^3D_1—$y^1P_1^\circ$	(0.53) 0.53, 1.10	(0.55) 0.52, 1.07
10.00	15	IV E	481.91	a^3F_3—$y^3P_2^\circ$		
3,507.90	4 hl		498.96			
3,493.97	2 h		612.58	$z^1P_1^\circ$—e^3P_2		
84.39	10 l		691.25	$z^3D_2^\circ$—f^3D_2	(0.00) 1.33	(0.04) 1.32
74.84	8 l		770.10	$x^3F_2^\circ$—g^1D_2		
66.46	1 h		839.64	$y^1D_2^\circ$—e^1P_1		
62.32	2 h		874.13			
60.31	5 l		890.90	$z^3P_2^\circ$—f^1F_3		
53.17	50	III E	950.63	a^3D_3—$x^1F_3^\circ$	(0.93) 0.37, 0.68, 1.00, 1.31, 1.63, 1.94	(—, —, 0.99) 0.34, 0.68, 1.01, 1.34, 1.67, 2.00
52.18	40	III E	958.94	a^1D_2—$y^1P_1^\circ$	(0.00) 0.95	(0.00) 0.95
51.12	3 l		28,967.83	$x^3P_1^\circ$—f^3P_1		
32.81	5		29,122.34	$z^3D_2^\circ$—f^3D_2		
27.57	8		166.85	$y^1F_3^\circ$—g^3D_3		
23.9	5		198.1	$x^3F_3^\circ$—f^1G_4		
22.44	2		210.57	$y^3D_1^\circ$—g^1D_2		
20.54	5 h		226.80	$y^1D_2^\circ$—g^3D_3		
11.76	20 hl		302.01	$x^3P_2^\circ$—f^3P_2	(0.00 w) 1.48	(0.05) 1.46
3,407.00	8 hl		342.95	$x^3P_0^\circ$—f^3P_1	(0.00) 1.50	(0.00) 1.47
3,398.29	2 h		418.15	$z^3D_3^\circ$—f^1D_2		
97.77	40 hl	V E	422.65	$y^1D_2^\circ$—f^3F_2	(0.24) 0.85	(0.23) 0.83
92.94	4 h		464.54	$z^3P_1^\circ$—g^3D_1		
90.40	4 h		486.61	$z^3P_2^\circ$—g^3D_1 $z^3P_2^\circ$—g^3D_2		
80.91	300	III E	569.36	a^3D_2—$x^3P_1^\circ$	(0.00, 0.37) 0.75, 1.11, 1.47	(0.00, 0.38) 0.76, 1.14, 1.52
76.33	50	III E	609.49	a^3D_2—$x^1F_3^\circ$	(0.00) 0.88	(0.00) 0.87

TABLE 4.—*The first spark spectrum of lanthanum* (*La II*)—Continued

λ_{air} I. A.	Intensity spark	Temperature class	ν_{vac} cm^{-1}	Term combinations	Zeeman effects	
					Observed	Computed
74.89	3		622.12			
51.89	3		825.37	$z^1F_3^\circ$—i^1D_2		
44.56	200	III E	890.73	a^3D_1—$x^3P_0^\circ$	(0.00) 0.53	(0.00) 0.52
37.49	300	III E	29,954.05	a^3D_2—$x^3P_2^\circ$	(0.00 w) 1.12 A[1]	(0.00) 1.06 A[1]
29.07	8		30,029.81	$z^3P_1^\circ$—g^3D_2		
26.21	5		055.63	$z^3P_2^\circ$—e^1P_1		
25.33	3		063.59	$z^3D_3^\circ$—g^3D_1		
10.62	4		197.16	$z^3D_3^\circ$—g^3D_3		
06.98	8	IV E	230.40	a^3F_4—$x^1F_3^\circ$	(0.00) 1.77 R	(0.00) 1.03
3,303.11	150	III E	265.82	a^3D_1—$x^3P_1^\circ$	(1.00) 0.51, **1.51**	(1.00) 0.52, 1.52
3,298.72	5 h		306.09			
97.15	3		320.52	z^3D_2—f^3G_3		
94.44	10		345.46	$x^3P_1^\circ$—f^3P_2		
83.95	8 h		442.39	$z^3P_2^\circ$—g^3D_3		
77.83	4		499.23	$x^3P_2^\circ$—g^3P_1		
67.31	3		597.43	$z^3P_1^\circ$—e^1P_1		
65.67	600	III E	612.79	a^3D_2—$x^3P_2^\circ$	(0.48, 0.80) 0.82, 1.17, **1.51**, 1.86	(0.34, 0.68) 0.80. **1.14**, **1.48**, 1.82
63.98	5		628.64	$z^3D_3^\circ$—g^3D_2		
53.41	10 h		728.15	$z^3D_1^\circ$—g^3D_1	(0.00) 0.65	(0.12) 0.61
49.35	80	III E	766.54	a^1D_2—$x^3P_1^\circ$	(0.00, 0.50) 0.46, 0.94, 1.44	(0.00, 0.53) 0.46, 0.99, **1.52**
45.13	150	III E	806.55	a^1D_2—$x^1F_3^\circ$	(0.00) 1.04	(0.00) 1.03
26.03	2		30,988.93	$z^1D_2^\circ$—f^3D_2		
24.71	1		31,001.62	$z^1H_5^\circ$—g^1G_4		
17.12	8 h		074.76	$x^3P_2^\circ$—g^3P_2		
12.56	5		118.86	$z^3P_2^\circ$—e^3S_1		
09.13	6		152.12	$z^3D_3^\circ$—g^3D_3		
08.13	6		161.83			
05.75	4		184.96	a^3F_3—$x^1F_3^\circ$		
3,204.55	3		196.64	$z^3D_2^\circ$—e^1P_1		
3,194.70	2		292.83	$z^3D_1^\circ$—g^3D_2		
93.02	25	IV E	309.29	a^3D_1—$x^3P_2^\circ$	(0.00, 0.96) 0.61, 1.58, **2.54.**	(0.00, 0.96) 0.52, 1.48, **2.44**
91.39	10 h		325.28	$x^3P_2^\circ$—h^3D_2		
74.88	10 hl		488.18	$x^3P_2^\circ$—h^3D_3		
66.26	2		573.90	$y^1D_2^\circ$—e^3P_2		
65.19	4		584.57	$y^3D_3^\circ$—h^1D_2		
60.56	3		630.84	$y^3P_2^\circ$—f^3P_1		
57.58	2		660.69	$z^3P_1^\circ$—e^3S_1		
56.35	2		673.02	$y^1P_1^\circ$—i^1D_2		
45.7	2 h		780.3	$z^3D_3^\circ$—f^3F_3		
42.76	40	IV E	809.98	a^1D_2—$x^3P_2^\circ$		
32.14	3		917.83	$x^3P_2^\circ$—g^3P_1		
30.25	2		937.10	$z^3P_2^\circ$—g^1D_2		
25.72	4 hl		31,983.39	$z^3P_2^\circ$—e^3P_1		
12.63	8 h		32,117.88	$x^3P_1^\circ$—g^3P_2		
08.46	8	IV E	160.97	a^3F_2—$x^3P_1^\circ$		
3,104.58	50	IV E	201.16	a^3F_2—$x^1F_3^\circ$	(0.00 w) 1.50 A[2]	(0.00) 1.56 A[2]
3,094.76	4 h		303.34			
88.53	4 h		368.49	$x^3P_1^\circ$—h^3D_2		
81.42	6 h		443.18	$z^3D_1^\circ$—f^3F_2		
75.51	4 h		505.52	$z^1F_3^\circ$—$^1D_2$?		
69.45	3		569.69	$z^3D_2^\circ$—e^3H_4		
68.96	4		575.09	$x^3P_0^\circ$—h^3D_1		
59.91	8		671.23	$z^1P_1^\circ$—f^3P_0		
54.02	6		734.24	$z^3D_3^\circ$—f^3F_3		
49.39	5		783.94	$z^3D_2^\circ$—f^3F_4		
45.63	1		824.41	$z^3G_5^\circ$—e^3H_4		
36.43	2		923.86	$z^3D_1^\circ$—e^3S_1		
35.80	1		32,930.69	$z^3G_4^\circ$—f^3G_4		
28.64	2		33,008.54	$y^3P_2^\circ$—f^3P_2		
25.88	4 ?		038.65	$z^3G_3^\circ$—f^3F_4		
22.26	5 hl		078.22	$z^3D_2^\circ$—g^1D_2		
18.95	6 hl		114.48			

TABLE 4.—*The first spark spectrum of lanthanum (La II)*—Continued

λ_{air} I. A.	Intensity spark	Temperature class	ν_{vac} cm^{-1}	Term combinations	Zeeman effects	
					Observed	Computed
07.32	5		242.54	$z^1D_2^1$—f^1F_3		
3,004.68	5 h		271.74			
2,985.76	2		482.57	$z^3G_4^1$—f^3F_3		
85.43	5		486.27	$x^3F_4^1$—h^1D_2		
84.33	3		498.61	$z^3D_3^1$—f^1G_4		
83.44	3		508.61	$z^3G_3^1$—f^3F_3		
76.83	3		583.01	$y^3P_2^0$—f^3P_1		
71.48	1		643.47	$y^3F_4^0$—f^3G_3		
66.55	4		699.38	$z^3G_5^1$—e^3H_5		
66.08	2		704.72	$z^1P_1^1$—f^3P_1		
62.90	15		740.89	$y^3O_3^0$—f^3P_1		
59.85	5		775.65	$z^3G_4^1$—e^3H_4		
58.71	1		788.67	$z^3D_1^1$—e^3P_1		
51.46	3		871.66	$y^3P_1^0$—i^1D_2		
50.50	50	V E	882.68	$z^1H_5^1$—e^3I_6	(0.00) 1.04	(0.00) 1.04
48.82	1		901.99	$y^3F_3^0$—f^1F_3		
43.56	6 hl		33,962.57	$z^1D_2^1$—f^3G_3		
39.64	3 h		34,007.85	$y^1P_1^0$—h^3D_1		
29.86	7		121.37	$y^3D_1^0$—f^3P_0		
25.15	5 h		176.31	$y^1P_1^0$—h^3D_2		
23.90	20		190.92	$y^3D_3^0$—f^3P_2	(0.00) 1.23?	(0.00) 1.17
13.60	2		311.78	$y^3F_2^0$—f^1D_2		
10.05	1		353.63	$y^1P_1^0$—$^1D_2$?		
2,905.53	4 hl		407.07	$z^1D_2^1$—e^1P_1		
2,899.80	4 hl		475.06	$y^3F_4^0$—g^3D_3		
97.76	5 hl		499.32	$y^3F_3^0$—g^3D_2		
93.08	60	V E	555.14	$z^3G_3^1$—e^3H_3	(0.00) 1.12	(0.00) 1.12
89.11	1		602.61	$z^1P_1^1$—i^1D_2		
85.13	50	V E	650.35	$z^3G_4^1$—e^3H_5	(0.00) 1.04	(0.00) 1.00
83.35	1		671.74	$z^3P_2^1$—g^3F_3		
80.65	40	V E	704.23	$z^3G_5^1$—e^3H_4	(0.00) 1.18	(0.00) 1.19
76.55	1		753.69			
74.28	3		781.14	$z^3G_3^1$—g^1D_2		
73.20	2		794.21	$z^1D_2^1$—g^3D_3		
67.47	2 h		863.74	$y^3P_2^0$—h^3D_1		
62.98	15 hl	V E	918.41	$z^3G_3^1$—f^3F_4		
62.37	6		925.85	$y^3F_2^0$—f^1F_3		
59.76	5		34,957.73	$y^3F_3^0$—g^3D_1		
55.90	50 hl	V E	35,004.97	$y^1F_3^0$—g^1G_4	(0.00) 1.13	(0.00) 1.13
53.72	4 h		031.71	$y^3P_2^0$—h^3D_2		
49.51	2 h		083.47			
48.34	6		097.88	$y^3F_3^0$—f_3G_4		
46.67	5		118.47	$y^3D_2^0$—f^3F_2		
43.67	4		155.51	$y^3D_1^0$—f^3P_1		
40.51	25 hl		194.62	$y^3P_2^0$—h^3D_2		
38.45	5 l		220.16	$y^3F_4^0$—f^3G_5		
32.53	5		293.77	$z^3D_2^1$—g^3F_2		
25.82	1		377.57	$y^1F_3^0$—h^1D_2		
25.51	5		381.45	$z^3D_3^1$—g^3F_3		
21.03	5		437.64	$y^1D_2^0$—h^1D_2		
19.73	2		453.97	$y^3F_3^0$—g^3D_3		
18.40	3		470.70	$z^1D_2^1$—e^3S_1		
15.36	6		509.00	$z^3F_2^1$—f^3D_2		
13.72	5		529.70	$z^3F_4^1$—f^3D_3		
13.05	3		538.16	$z^1G_4^1$—f^1F_3		
09.35	2		584.96	$z^3F_3^1$—f^3D_1		
08.39	150	V E	597.13	b^1D_2—$x^1P_1^1$	(0.00) 1.04	(0.00) 1.04
07.20	1		612.22	$x^3F_3^1$—i^1D_2		
05.58	5		632.78	$z^3G_3^1$—f_1G_4		
2,804.55	4		645.86	$y^3F_3^0$—f^3G_3		
2,798.56	40 hl	V E	722.15	$z^3D_3^1$—g^3F_4	(0.00) 1.08	(0.00) 1.08
96.40	5		749.75	$z^1F_3^1$—f^1D_2		
91.51	25		812.37	$z^3D_2^1$—g^3F_3	(0.00) 1.04 R	(0.00) 1.03
81.25	1		944.47	$z^1D_2^1$—f^3F_3		
80.23	20		957.66	$z^3D_1^1$—g^3F_2		

TABLE 4.—*The first spark spectrum of lanthanum (La II)*—Continued

λ_{air} I. A.	Intensity spark	Temperature class	ν_{vac} cm^{-1}	Term combinations	Zeeman effects	
					Observed	Computed
79.78	10		963.48	$y^3D_3^0$—g^3P_2		
78.76	10		35, 976.68	$z^3G_3^0$—g^3F_4		
73.86	1		36, 040.23	$z^1P_1^0$—g^3P_0		
67.40	8		124.35	$y^3P_2^0$—g^3P_2		
61.10	5		206.77	$y^3P_1^0$—h^3D_1		
60.51	3		214.51	$y^3D_3^0$—h^3D_2		
59.14	3		232.49	$z^3H_4^0$—e^3H_5		
58.65	3		238.93	$y^1P_1^0$—f^1S_0		
55.57	1		279.43	$z^1P_1^0$—g^3P_1		
52.84	10		315.41	$y^3D_2^0$—g^3P_1		
48.31	8		375.26	$y^3P_1^0$—h^3D_2		
36.90	2		526.90	$z^3H_5^0$—e^3H_4		
36.41	3		533.44	$y^3D_1^0$—f^3P_2		
32.40	10		587.05	$z^3G_4^0$—g^3F_3		
27.5	2		652 8	$z^3P_2^0$—h^1D_2		
26.48	1		666.49	$y^1D_2^0$—f^3P_1		
21.45	2		734.25	$z^1G_4^0$—f^3G_4		
15.43	10 hl		815.68	$y^3P_0^0$—h^3D_1		
12.51	1		855.32	$z^1P_1^0$—g^3P_2		
09.92	3		890.54	$y^3D_2^0$—g^3P_2		
06.49	2		937.29	$z^1P_1^0$—h^3D_1		
2,702.13	8		36, 996.88	$z^3G_3^0$—g^3F_3		
2,695.47	35		37, 088.29	$z^3H_5^0$—e^3H_5		
94.21	5		105.64	$z^1P_1^0$—h^3D_2		
91.60	1		141.62	$y^3D_2^0$—h^3D_2		
87.75	2		194.81	$z^3P_1^0$—h^1D_2		
81.49	10		281.64	$z^3H_4^0$—e^3H_4		
79.87	4 h		304.17	$y^3D_2^0$—h^3D_3		
75.66	5		362.87	$z^3D_3^0$—h^1D_2		
73.74	3		389.70	$z^3P_1^0$—f^3P_0		
72.90	30		401.45	$z^3H_5^0$—e^3H_5		
72.06	2		413.20			
70.05	2		441.37	$x^3F_3^0$—g^3P_2		
66.54	3		490.65	$y^3D_1^0$—g^3P_0		
66.18	6		495.71	$z^3H_4^0$—f^3F_4		
65.62	4		503.59	$y^1F_3^0$—i^1D_2		
64.75	3		515.83	$z^3G_3^0$—g^3F_3		
62.73	1 h		544.29			
61.66	3		559.38	$z^1F_3^0$—f^3G_4		
61.36	4		563.61	$y^1D_2^0$—i^1D_2		
49.61	1		730.18	$y^3D_1^0$—g^3P_1		
47.36	4		762.25	$z^3F_3^0$—f^1F_3		
44.70	1		800.23	$y^3F_3^0$—f^1G_4		
42.27	1		834.96	$z^1G_4^0$—f^3G_5		
40.15	1		865.37	$x^3F_2^0$—g^3P_2		
39.00	5		881.87	$z^3P_2^0$—f^3P_1		
36.66	1		915.48	$z^1F_3^0$—g^3D_3		
31.94	8		983.47	$y^1F_3^0$—f^3P_2		
31.52	4		3, 7989.54	$z^3F_4^0$—f^1F_3		
20.01	7		3, 8156.42	$z^3H_4^0$—e^3H_5		
17.29	1		196.07	$z^3G_4^0$—g^1G_4		
16.32	7 hl		210.23	$z^3H_4^0$—f^1G_4		
13.09	4		257.46	z^3H_5—e^3H_6		
10.34	150		297.76	a^1S_0—$x^1P_1^0$		
04.18	1		388.35	$y^3D_1^0$—h^3D_1		
02.87	1		407.66			
01.79	5		423.60	$z^3P_1^0$—f^3P_1		
00.86	2		437.34	$y^3P_1^0$—f^1S_0		
2,600.33	4		445.18	$z^3P_0^0$—f^3P_1		
2,596.32	3		504.55	$z^1D_2^0$—g^3F_2		
96.08	20		508.11	$z^1G_4^0$—e^3H_4		
92.87	3 h		555.78	$y^3D_1^0$—h^3D_2		
86.35	10		652.97	$z^3D_1^0$—f^3P_0		
82.96	8		703.70	$y^3F_4^0$—g^3F_3		
82.55	6		709.85	$z^3F_2^0$—f^3G_3		

TABLE 4.—*The first spark spectrum of lanthanum (La II)*—Continued

λ_{air} I. A.	Intensity spark	Temperature class	ν_{vac} cm^{-1}	Term combinations	Zeeman effects	
					Observed	Computed
80.82	8 hl		735.79	$z^4F^\circ_{\frac{7}{2}}$—f^4G_5		
77.92	2		779.36	$z^3P^\circ_2$—i^1D_2		
73.47	2 h		846.42			
66.09	10 hl		38,958.13	$z^3F^\circ_4$—f^3G_4		
61.84	20 l		39,022.75	$z^1D^\circ_2$—g^3F_3 $z^3D^\circ_{\frac{3}{2}}$—f^3P_1		
60.37	50		045.15	$y^3F^\circ_4$—g^3F_4		
58.99	3		066.21	$z^1F^\circ_3$—f^3F_3		
58.72	2		070.33			
53.41	3 h		151.57	$y^1P^\circ_1$—g^1S_0		
52.60	7		164.00	$y^3F^\circ_3$—g^3F_2		
52.36	2		167.68	$z^1P^\circ_1$—f^1S_0		
46.40	20 hl		259.35	$z^3P^\circ_{\frac{3}{2}}$—f^3P_2		
42.40	6		321.11	$z^3P^\circ_{\frac{3}{2}}$—i^1D_2		
41.60	4		333.49	$z^1F^\circ_{\frac{7}{2}}$—e^3H_4		
38.40	2		383.07	$z^1G^\circ_4$—e^3H_5		
36.76	3		408.53	$z^3F^\circ_4$—e^3H_4		
34.98	6		436.21	$z^1G^\circ_4$—f^1G_4		
33.14	15		464.84	a^3P_2—$x^1P^\circ_1$		
31.60	8		488.84	$z^3D^\circ_{\frac{3}{2}}$—i^1D_2		
30.26	1		509.76	$z^3F^\circ_2$—f^3F_2		
27.84	3		547.58	$z^1F^\circ_{\frac{7}{2}}$—f^3F_4		
23.07	5 hl		622.34	$z^3F^\circ_4$—f^3F_4		
19.22	50		682.89	$y^3F^\circ_3$—g^3F_3		
15.79	4		736.99	$z^3F^\circ_2$—f^3F_2		
14.59	3		755.95	$y^1F^\circ_3$—g^3P_2		
2,501.18	15 hl		969.08	$z^3D^\circ_3$—f^3P_2		
2,499.69	1		39,992.91			
95.82	2		40,054.91			
94.90	1		069.68			
87.59	40		187.42	$y^3F^\circ_2$—g^3F_2		
83.00	2hl		261.71	$z^1F^\circ_{\frac{7}{2}}$—f^1G_4		
79.85	10 l		312.85	$y^3F^\circ_4$—g^1G_4		
74.50	3		400.00	$z^3D^\circ_{\frac{3}{2}}$—f^3P_2		
72.44	10		433.65	$z^3H^\circ_4$—g^3F_4		
71.90	20		442.49	a^3P_0—$x^1P^\circ_1$		
71.06	5		456.23	$z^3P^\circ_{\frac{5}{2}}$—g^3P_1		
70.55	3		464.58	$z^3F^\circ_3$—f^3F_3		
68.11	1		504.58			
58.15	2		668.69	$x^3F^\circ_4$—i^3D_3		
55.88	10		706.28	$y^3F^\circ_2$—g^3F_3		
54.30	1		732.48	$z^3F^\circ_{\frac{7}{2}}$—e^3H_4		
52.73	8		758.55	$z^3P^\circ_1$—g^3P_0		
51.59	2		777.50			
45.56	10 h		878.04			
43.14	2 h		918.53	$y^3D^\circ_3$—i^3D_3		
42.80	3		924.22			
39.08	2		986.63			
38.42	10		40,997.82	$z^3P^\circ_1$—g^3P_1		
38.02	20		41,004.45	$z^1D^\circ_2$—h^1D_2		
37.14	10		019.26	$z^3P^\circ_0$—g^3P_1		
36.42	15		031.37	$z^3P^\circ_2$—g^3P_2		
31.40	6 h		116.08			
24.53	2 h		232.58			
21.61	5 h		282.29	$z^3P^\circ_{\frac{3}{2}}$—h^3D_2		
20.01	5 hl		309.58			
17.61	3 h		350.59	$y^3P^\circ_1$—g^1S_0		
12.08	2 h		445.38	$z^3P^\circ_{\frac{3}{2}}$—h^3D_3		
10.10	5 hl		479.43			
07.79	5 hl		519.22			
04.65	6		573.43	$z^3P^\circ_1$—g^3P_2		
03.29	7		596.96	$z^3D^\circ_{\frac{3}{2}}$—g^3P_1		
2,401.46	2 h		628.66			
2,399.64	20 hl		660.22	$z^1G^\circ_4$—g^3F_4		
98.70	3 h		676.55			
97.26	7 hl		701.57	$z^3H^\circ_4$—g^1G_4		

TABLE 4.—*The first spark spectrum of lanthanum (La II)*—Continued

λ_{air} I. A.	Intensity spark	Temperature class	ν_{vac} cm^{-1}	Term combinations	Zeeman effects	
					Observed	Computed
94.98	4		741.27	$z^3D_3^3$—g^3P_2		
93.27	2 h		771.10			
89.84	3 hl		831.04			
88.96	2		846.45			
86.26	2		893.80			
84.28	3 h		41,928.58			
75.63	2 h		42,081.24	$z^1P_1^1$—g^1S_0		
70.47	2		172.84	$z^3D_2^2$—g^3P_2		
69.18	2		195.79			
65.50	3		261.43	$z^3D_1^1$—g^3P_1		
58.02	3 h		395.48			
56.10	1 h		430.02			
55.81	5 h		435.24			
53.40	2		478.70			
53.03	1		485.48	$z^1F_3^3$—g^3F_4		
51.93	1		505.24			
48.86	2		560.79	$z^3F_4^4$—g^3F_4		
41.85	4		688.18	$y^3F_3^3$—h^1D_2		
25.75	20 hl		42,928.29	$z^1G_4^4$—g^1G_4		
22.78	3 h		43,038.62			
19.44	20		100.59	a^3D_2—$x^1P_1^1$		
17.82	20 hl		130.71	$z^1D_2^2$—i^1D_2		
2,311.45	1		249.56			
2,293.47	2 h		588.59			
92.32	3		610.45	$z^1D_2^2$—f^3P_2		
80.94	4 h		828.01	$z^3H_5^5$—e^1I_6		
76.06	1 h		43,921.97			
65.53	3		44,125.90	$z^1F_3^3$—h^1D_2		
56.77	50		297.36	a^1D_2—$x^1D_2^2$		
30.74	7		44,814.20	$y^3F_2^2$—i^1D_2		
07.08	1		45,294.56	$y^3F_2^2$—f^3P_2		
2,202.72	1		383.38	$z^1D_2^2$—g^3P_2		
2,195.91	4		524.94	$z^3F_3^3$—h^1D_2		
90.67	1		633.82	$z^1D_2^2$—h^3D_2		
87.87	40		45,692.22	a^3F_2—$x^1P_1^1$		
63.66	20 hl		46,203.12			
61.36	4		252.58	$z^1F_3^3$—i^1D_2		
42.81	20 hl		46,642.94			

IV. THE SPECTRUM OF NEUTRAL LANTHANUM (La I)

As in Sc and Y, the normal state of the neutral La atom is represented by a doublet-D term associated with the electron configuration ds^2. In each case, the next lowest energy is represented by a quartet-F term arising from d^2s, but in La it is only about one-third as high as in Sc or Y. The remaining metastable low terms also come from d^2s, and are exactly analogous to those in Sc and Y. The ^{2}G is narrow and inverted in all three spectra, and the predicted ^{2}S has been found in none. The odd levels are very numerous, and it is difficult to group them into terms. Indeed, parts of the tangle could not have been unraveled without the clues obtained from the new measurements of Zeeman effects.

The triads of quartet terms obtained by the addition of a $6p$ electron to the ^{3}D, ^{3}F, and ^{3}P terms of La II can be securely identified. They all lie lower than the corresponding terms of Y I. Three additional odd quartet terms, x^4F°, y^4G°, and w^4D°, at higher levels can come only from the addition of a $4f$ electron to the same limits. The doublet terms arising from the addition of a $6p$ electron to the various limits have also been certainly or probably identified by the intensities of their combinations and comparison of their levels with Y I. A number of supernumerary doublet terms must also arise from the $4f$ electron, which in this case is less firmly bound than the $6p$.

Many of the numbered odd levels which have not been grouped into terms are probably of similar origin. The high terms, 10° to 15°, probably arise from electrons of higher total quantum number.

The high even terms give much less conspicuous combinations in La I than in Sc I or Y I, and only a few of them have been found—but enough to give the ionization potential. The unassigned even levels have been numbered from 30 onward. If the strong bands of LaO in the yellow and red could be eliminated more such terms could probably be identified, and some fairly strong high temperature arc lines classified.

Table 5 gives the terms of the La I spectrum in the same general form as Table 3 does for La II. The configuration from which each term is believed to arise is given opposite its lowest component. For the odd terms, the probable parent terms in La II are indicated.

TABLE 5.—*Relative terms in the La I spectrum*

Electron configuration	Term	Level	Level separation	g			Combinations
				Adapted weight		Landé	
ds^2	$a^3D_{1\frac{1}{2}}$	0.00	1,053.20	0.790	6	0.800	z^4F°, z^4D°, z^2D°, z^2F°, z^2P°, y^2F°, z^4P°, z^4G°, y^2D°, y^2P°, y^4F°, x^2F°, z^2G°, y^4D°, 3°, x^4D°, w^2F°, v^2F°, z^4S°, x^2D°, x^2F°, x^2P°, y^4P°, y^4G°, w^2P°, u^2F°, t^2F°, w^2D°, v^2D°, w^4D°, 6°, 7°, 8°, s^2F°, 9°, r^2F°, u^2D°, v^2P°, 10°, 11°.
	$a^2D_{2\frac{1}{2}}$	1,053.20		1.203	14	1.200	
d^2s	$a^4F_{1\frac{1}{2}}$	2,668.20	341.81	.411	20	.400	z^4F°, z^4D°, z^2D°, z^2F°, z^2P°, y^2F°, z^4P°, z^4G°, y^2D°, y^2P°, y^4F°, x^2F°, z^2G°, y^4D°, 7°, 2°, 3°, w^2F°, x^4D°, 4°, v^2F°, z^4S°, x^2D°, x^4F°, x^2P°, y^4P°, y^4G°, y^2G°, 12°, 13°, 14°, 15°.
	$a^4F_{2\frac{1}{2}}$	3,010.01	484.57	1.032	11	1.029	
	$a^4F_{3\frac{1}{2}}$	3,494.58	627.03	1.222	10	1.238	
	$a^4F_{4\frac{1}{2}}$	4,121.61		1.327	8	1.333	
d^2s	$a^4P_{\frac{1}{2}}$	7,231.36	259.10	2.706	10	2.667	z^4P°, y^2F°, z^4G°, y^2D°, x^2F°, z^2S°, x^4D°, 3°, 4°, w^2F°, z^4S°, x^2D°, x^4F°, y^4P°, x^2P°, w^2D°, t^2F°, w^4D°, v^2D°, 6°, 7°, 8°, s^2F°, 9°.
	$a^4P_{1\frac{1}{2}}$	7,490.46	189.48	1.69	6	1.733	
	$a^4P_{2\frac{1}{2}}$	7,679.94		1.54	4	1.600	
d^2s	$a^2F_{2\frac{1}{2}}$	7,011.90	1,040.25	.90	$3\frac{1}{2}$	.857	y^2F°, z^4G°, z^4P°, y^2D°, y^4F°, x^2F°, z^2G°, y^4D°, 1°, 2°, w^2F°, v^2F°, x^2D°, x^4F°, x^4D°, v^2F°, y^4P°, y^4G°, y^2G°, w^2P°, u^2F°, t^2F°, w^2D°, v^2D°, w^4D°, 7°, s^2F°, r^2F°, u^2D°, 10°, 11°.
	$a^2F_{3\frac{1}{2}}$	8,052.15		1.13	5	1.143	
d^2s	$b^2D_{1\frac{1}{2}}$	8,446.03	737.74	.89	3	.800	z^4G°, z^4P°, y^2D°, y^2P°, y^4F°, z^2S°, x^4D°, 4°, z^2F°, z^4S°, x^2D°, x^4F°, x^2P°, y^4P°, w^2P°, w^2F°, 5°, w^2D°, t^2F°, s^2D°, w^4D°, 8°, s^2F°, 9°, r^2F°, u^2D°.
	$b^2D_{2\frac{1}{2}}$	9,183.77		1.29	3	1.200	
d^2s	$a^2P_{\frac{1}{2}}$	9,044.21	675.23	.67	1	.667	y^2D°, y^2P°, y^4F°, x^2F°, z^2S°, x^4D°, w^2F°, 6°, s^2F°, x^2D°, x^4F°, x^2P°, y^4P°, w^2P°, 5°, w^2D°, w^2P°, t^2D°, u^2D°, v^2P°.
	$a^2P_{1\frac{1}{2}}$	9,719.44		1.32	2	1.333	
d^2s	$a^2G_{4\frac{1}{2}}$	9,919.94	−41.02	1.12	1	1.111	y^4F°, x^2F°, z^2G°, y^2G°, w^2F°, z^2H°, x^4F°, y^2G°, w^2F°, y^4G°, w^2D°, t^2F°, s^2F°, 9°, r^2F°, y^2H°.
	$a^2G_{3\frac{1}{2}}$	9,960.96		.91	1	.889	
$a^3D.p$	$z^4F^\circ_{1\frac{1}{2}}$	13,260.36	370.72				a^2D, a^4F, 31, 32, 35, e^4F, e^4D.
	$z^4F^\circ_{2\frac{1}{2}}$	13,631.08	1,388.47	1.08		1.029	
	$z^4F^\circ_{3\frac{1}{2}}$	15,019.55	1,223.70	1.21		1.238	
	$z^4F^\circ_{4\frac{1}{2}}$	16,243.25					
$a^3D.p$	$z^4D^\circ_{\frac{1}{2}}$	14,095.70	613.26				a^2D, a^4F, 31, 32, 33, 34, e^4F, e^4D.
	$z^4D^\circ_{1\frac{1}{2}}$	14,708.96	794.71				
	$z^4D^\circ_{2\frac{1}{2}}$	15,503.67	595.61				
	$z^4D^\circ_{3\frac{1}{2}}$	16,099.28					
$a^1D.p$	$z^2D^\circ_{2\frac{1}{2}}$	14,804.10	−227.55	1.08		1.200	a^2D, a^4F, 31, e^2F.
	$z^2D^\circ_{1\frac{1}{2}}$	15,031.65		.97		.800	
$a^1D.p$	$z^2F^\circ_{2\frac{1}{2}}$	15,196.80	1,341.64	.90		.857	a^2D, a^4F, e^4D, e^2F.
	$z^2F^\circ_{3\frac{1}{2}}$	16,538.44		1.19		1.143	
$a^1S.p$	$z^2P^\circ_{\frac{1}{2}}$	15,219.90	1,060.30				a^2D, a^4F.
	$z^2P^\circ_{1\frac{1}{2}}$	16,280.20					

TABLE 5.—*Relative terms in the La I spectrum*—Continued

Electron configuration	Term	Level	Level separation	g		Combinations
				Adapted weight	Landé	
$a^2D.p$	$y^2F^0_{3½}$	16,856.82	1,053.36	0.83	0.857	a^2D, a^4F, a^2F, a^4P.
	$y^2F^0_{2½}$	17,910.18		1.08	1.143	
$a^2D.p$	$z^4P^0_{½}$	17,567.56	229.74			a^2D, a^4F, a^2F, a^4P, b^2D.
	$z^4P^0_{1½}$	17,797.30	359.70			
	$z^4P^0_{2½}$	18,157.00		1.20	1.600	
$a^2F.p$	$z^4G^0_{3½}$	17,947.16	656.79	1.07	.571	a^2D, a^4F, a^2F, a^4P, b^2D, e^4F, 35.
	$z^4G^0_{4½}$	18,603.95	525.39	1.06	.984	
	$z^4G^0_{2½}$	19,129.34	988.06	1.15	1.172	
	$z^4G^0_{5½}$	20,117.40		1.27	1.273	
$a^2D.p$	$y^2D^0_{1½}$	18,172.39	1,207.05	.83	.800	a^2D, a^4F, a^2F, a^4P, b^2D, a^2P, e^4F.
	$y^2D^0_{2½}$	19,379.44		1.19	1.200	
$a^2D.p$	$y^2P^0_{1½}$	20,019.00	−178.38	1.05	1.333	a^2D, a^4F, b^2D, a^2P, e^4F.
	$y^2P^0_{½}$	20,197.38		.60	.667	
$a^4F.p$	$y^4F^0_{1½}$	20,083.02	255.28	.78	.400	a^2D, a^4F, a^2F, a^2P, b^2D, a^2G, e^4F, e^2F.
	$y^4F^0_{2½}$	20,338.30	425.01	1.01	1.029	
	$y^4F^0_{3½}$	20,763.31	620.75	1.18	1.238	
	$y^4F^0_{4½}$	21,384.06		1.28	1.333	
$a^2F.p$	$x^2F^0_{2½}$	20,972.22	690.39	.90	.857	a^2D, a^4F, a^2F, a^4P, a^2P, a^2G, e^2F.
	$x^2F^0_{3½}$	21,662.61		1.13	1.143	
$a^2F.p$	$z^2G^0_{3½}$	21,447.92	837.93	1.08	.889	a^2D, a^4F, a^2F, a^2G, e^2F.
	$z^2G^0_{4½}$	22,285.85		1.13	1.111	
$a^2F.p$	$y^4D^0_{½}$	22,246.64	192.73	.03	.000	a^2D, a^4F, a^2F.
	$y^4D^0_{1½}$	22,439.37	364.89	1.21	1.200	
	$y^4D^0_{2½}$	22,804.26	499.05	1.35	1.371	
	$y^4D^0_{3½}$	23,303.31		1.22	1.429	
	$1^0_{1½}$	23,221.16		1.11		a^4F, a^2F.
	$2^0_{2½}$	23,466.85		1.12	1.111	a^4F, a^2F, a^2G.
$a^2P.p$	$z^2S^0_{½}$	23,260.90		1.87	2.000	a^4P, b^2D, a^2P.
	$3^0_{½}$	23,549.42				a^4F, a^4P.
	$4^0_{½}$	24,173.86		.72		a^4F, a^4P, b^2D, a^2P.
$a^2P.p$	$x^4D^0_{½}$	23,528.38	176.38	.00	.000	a^2D, a^4F, a^2F, a^4P, b^2D, a^2P.
	$x^4D^0_{1½}$	23,704.76	341.30	1.15	1.200	
	$x^4D^0_{2½}$	24,046.06	1,037.36	1.22	1.371	
	$x^4D^0_{3½}$	25,083.42		1.41	1.429	
$a^2D.f$	$w^2F^0_{3½}$	23,875.00	534.70	.94	.857	a^2D, a^4F, a^2F, a^4P, a^2P, a^2G.
	$w^2F^0_{2½}$	24,409.70		1.17	1.143	
	$v^2F^0_{3½}$(?)	24,507.89	870.57	1.20	.857	a^2D, a^4F, a^2F, a^4P, b^2D, a^2P.
	$v^2F^0_{2½}$(?)	25,378.46		1.13	1.143	
$a^2P.p$	$z^4S^0_{1½}$	24,639.27		1.81	2.000	a^2D, a^4F, a^4P, b^2D.
$a^2F.p$	$z^2D^0_{1½}$	24,762.62	455.63	.88	.800	a^2D, a^4F, a^2F, a^4P, b^2D.
	$z^2D^0_{2½}$	25,218.25		1.25	1.200	
$a^4F.f$	$x^4F^0_{½}$	24,910.39	73.94	.73	.400	a^2D, a^4F, a^2F, a^2G.
	$x^4F^0_{1½}$	24,984.33	396.00	1.11	1.029	
	$x^4F^0_{2½}$	25,380.33	616.94	1.23	1.238	
	$x^4F^0_{4½}$	25,997.27		1.36	1.333	
$a^2G.p$	$z^2H^0_{4½}$	25,089.50	785.18	.94	.909	a^4F, a^2G.
	$z^2H^0_{5½}$	25,874.68				
$a^2D.p$	$x^2P^0_{½}$	25,453.92	496.47	.92	.667	a^2D, a^4F, a^4P, b^2D, a^2P.
	$x^2P^0_{1½}$	25,950.39		1.41	1.333	z^2D^0, z^4F^0, z^4D^0.
	31	25,568.49				z^2D^0, z^4D^0, z^4F^0.
	$32_{2½}$	25,881.53				
$a^2P.p$	$y^4P^0_{½}$	25,616.90	26.12	2.29	2.667	a^2D, a^4F, a^2F, a^4P, b^2D, a^2P.
	$y^4P^0_{1½}$	25,643.02	695.88	1.61	1.733	
	$y^4P^0_{2½}$	26,338.90		1.54	1.600	
$a^2F.f$	$y^4G^0_{3½}$	27,022.60	432.74	.57	.571	a^2D, a^4F, a^2F, a^2G.
	$y^4G^0_{4½}$	27,455.34	633.84	.99	.984	
	$y^4G^0_{5½}$	28,089.18	654.03	1.16	1.172	
	$y^4G^0_{2½}$	28,743.21		1.29	1.273	

TABLE 5.—*Relative terms in the La I spectrum*—Continued

Electron configuration	Term	Level	Level separation	g		Combinations
				Adapted weight	Landé	
$a^1G.\ p$	$y^2G^\circ_{3½}$	27,132.50	487.19	0.95	0.889	$a^4F,\ a^2F,\ a^2G.$
	$y^2G^\circ_{4½}$	27,619.69		1.12	1.111	
$b^1D.\ p$	$w^2P^\circ_{1½}$	27,225.27		1.34	1.333	$a^2D,\ a^2F,\ b^2D,\ a^2P.$
$b^1D.\ p$	$u^2F^\circ_{2½}$	27,393.00	646.54	.90	.857	$a^2D,\ a^2F,\ a^2G.$
	$u^2F^\circ_{3½}$	28,039.54		1.13	1.143	
f	$t^2F^\circ_{2½}$	27,669.38	873.72	.88	.857	$a^2D,\ a^2F,\ a^2G.$
	$t^2F^\circ_{3½}$	28,543.10		1.00	1.143	
	$5i_{5½}$	27,749.05				$b^2D,\ a^2P.$
$b^1D.\ p$	$w^2D^\circ_{1½}$	27,968.53	537.86	.91	.800	$a^2D,\ a^2F,\ a^4P,\ b^2D,\ a^2P.$
	$w^2D^\circ_{2½}$	28,506.39				
$a^3P.\ f$	$w^4D^\circ_{½}$	28,893.47	306.06	0.00	0.000	$a^2D,\ a^2F,\ a^4P,\ b^2D.$
	$w^4D^\circ_{1½}$	29,199.53	302.64	1.15	1.200	
	$w^4D^\circ_{2½}$	29,502.17	392.74			
	$w^4D^\circ_{3½}$	29,894.91		1.29	1.429	
f	$x^2D^\circ_{1½}$	28,971.82	803.75	.94	.800	$a^2D,\ a^2F,\ a^4P,\ b^2D,\ a^2P.$
	$x^2D^\circ_{2½}$	29,775.57		1.13	1.200	
	33	29,461.33				$z^4D^\circ.$
	$6^\circ_{½}$	29,564.92				$a^2D,\ a^4P,\ b^2D,\ a^2P.$
	$7i_{5½}$	29,936.73		1.54		$a^2D,\ a^2F,\ a^4P.$
	$8i_{6½}$	30,417.47		1.54		$a^2D_1\ a^4P_1\ b^2D.$
	34(?)	29,594.81				$z^4D^\circ.$
$a^3F.s$	$e^4F_{1½}$	29,874.89	479.43			$z^4F^\circ,\ z^4D^\circ,\ y^4F^\circ,\ z^4G^\circ.$
	$e^4F_{2½}$	30,354.32	705.37			
	$e^4F_{3½}$	31,059.69	864.21			
	$e^4F_{4½}$	31,923.90				
$a^1G.p$	$s^2F^\circ_{2½}$	30,788.40	176.42			$a^2D,\ a^4P,\ a^2F,\ b^2D,\ a^2G.$
	$s^2F^\circ_{3½}$	30,964.82		1.18	1.143	
	$9i_{6½}$	30,896.88		1.45		$a^2D,\ a^4P,\ b^2D,\ a^2G.$
$a^3F.s$	$c^2F_{3½}$	31,119.08	989.50			$z^2D^\circ,\ z^2F^\circ,\ y^4F^\circ,\ z^2G^\circ.$
	$c^2F_{3½}$	32,108.58				
$a^3D.s$	$e^4D_{3½}$	31,287.65				$z^4F^\circ,\ z^4D^\circ,\ z^2F^\circ.$
f	$r^2F^\circ_{3½}$	31,477.16		.88	.857	$a^2D,\ a^2F,\ b^2D,\ a^2G.$
	$r^2F^\circ_{4½}$	32,140.60		1.18	1.143	
$a^3P.p$	$u^2D^\circ_{1½}$	31,751.68	741.12	.82	.800	$a^2D,\ a^2F,\ b^2D,\ a^2P.$
	$u^2D^\circ_{2½}$	32,492.80		1.17	1.200	
$a^3P.p$	$v^2P^\circ_{½}$	32,290.25	913.95	1.26	1.333	$a^2D,\ b^2D,\ a^2P.$
	$v^2P^\circ_{1½}$	33,204.20				
$a^1G.f$	$y^2H^\circ_{4½}$	32,410.76	107.36	.93	.909	$a^2G.$
	$y^2H^\circ_{5½}$	32,518.12		1.11	1.091	
	35	33,286.50				$z^4F^\circ,\ z^2F^\circ,\ y^2F^\circ,\ z^4G^\circ.$
	10°	36,722.38				$a^2D,\ a^2F.$
	11°	37,731.90				$a^2D,\ a^2F.$
	12°(?)	39,597.58				$a^4F.$
	13°	39,631.27				$a^4F.$
	14°	40,322.45				$a^4F.$
	15°	40,343.40				$a^4F.$

The spectral terms and combinations for La I are represented diagrammatically in Figure 2, which may be compared with corresponding diagrams for Sc I and Y I spectra in publications already referred to.[25]

Complete details of lines regarded as characteristic of neutral lanthanum atoms are given in Table 6, the arrangement and notation being the same as that in Table 4. Here again the Zeeman patterns computed from the adopted g values are almost always in good agreement with observation.

[25] See footnotes 2 and 3, p. 625.

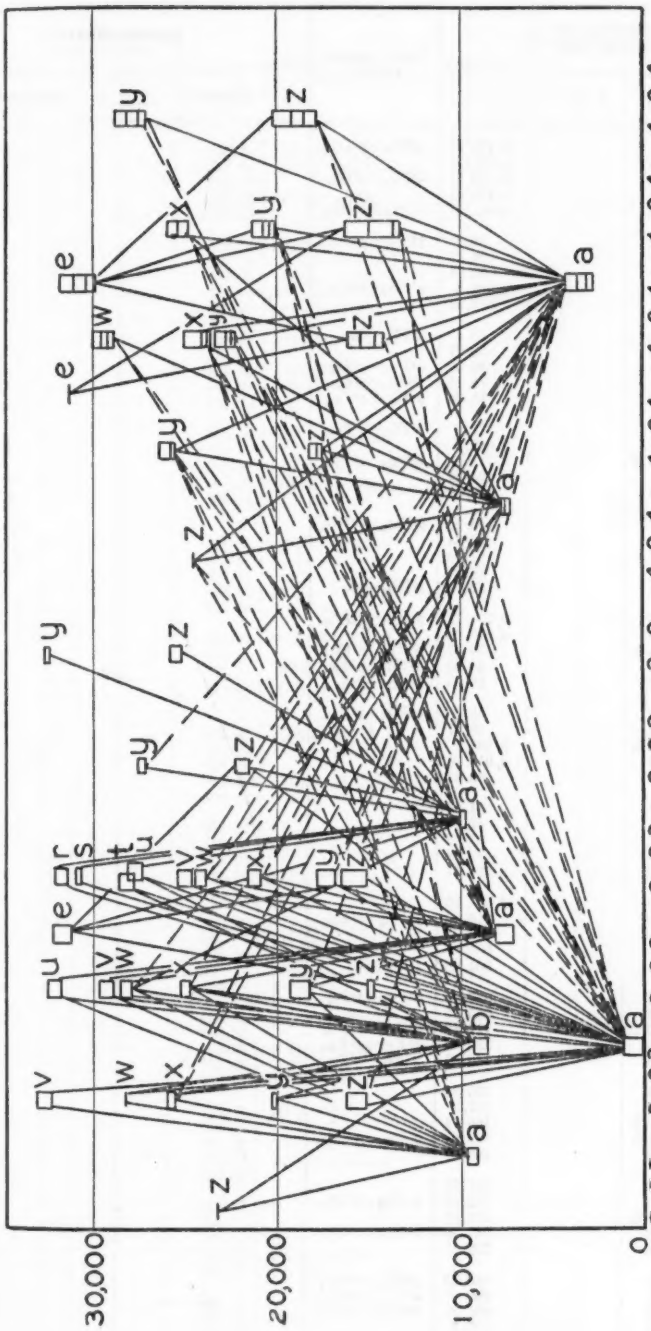

FIGURE 2.—*Terms and combinations in the La I spectrum*

TABLE 6.—*The arc spectrum of lanthanum (La I)*

λ air I. A.	Intensities, temperature class		ν vac cm^{-1}	Term combination	Zeeman effects	
	B. S.	K. & C.			Observed	Computed
10, 952. 0	1		9, 128. 25	$a^2P_{1\frac{1}{2}}$—$y^3D^0_{1\frac{1}{2}}$		
10, 739. 66	5		9, 308. 73			
10, 612. 56	10		9, 420. 21	$b^3D_{2\frac{1}{2}}$—$z^4G^0_{3\frac{1}{2}}$		
10, 552. 41	6		9, 473. 91			
10, 522. 09	10		9, 501. 21	$b^3D_{1\frac{1}{2}}$—$z^4G^0_{2\frac{1}{2}}$		
10, 483. 0	2		36. 6	$y^4F^0_{3\frac{1}{2}}$—$e^4F_{1\frac{1}{2}}$		
61. 69	15		56. 07			
50. 82	20		66. 01			
23. 4	1		9, 591. 2	$y^4F^0_{1\frac{1}{2}}$—$e^4F_{2\frac{1}{2}}$		
10, 409. 55	3		9, 603. 93			
10, 372. 4	1		38. 4	$z^4F^0_{1\frac{1}{2}}$—32		
57. 70	20		52. 01			
49. 08	40		60. 05	$a^2P_{1\frac{1}{2}}$—$y^3D^0_{2\frac{1}{2}}$		
37. 20	3		71. 15	$z^3G^0_{3\frac{1}{2}}$—$e^3F_{2\frac{1}{2}}$		
32. 40	2		75. 64	$y^4F^0_{2\frac{1}{2}}$—$e^4F_{2\frac{1}{2}}$		
30. 3	1		77. 6	$y^2P^0_{1\frac{1}{2}}$—$e^4F_{1\frac{1}{2}}$		
10, 318. 2	2		9, 689. 0			
10, 294. 68	10 d		9, 711. 09	$b^3D_{1\frac{1}{2}}$—$z^4P^0_{2\frac{1}{2}}$		
85. 64	3		21. 52			
81. 34	10		23. 69			
78. 52	3		26. 37	$b^3D_{1\frac{1}{2}}$—$y^3D^0_{1\frac{1}{2}}$		
74. 85	10		29. 84			
34. 78	2		67. 93			
23. 76	1		78. 46			
19. 83	3		82. 22	$z^4D^0_{3\frac{1}{2}}$—32		
10, 209. 85	2		9, 791. 78	$y^4F^0_{1\frac{1}{2}}$—$e^4F_{1\frac{1}{2}}$		
10, 184. 60	20		9, 816. 06			
77. 74	6 h		22. 67	$z^3G^0_{3\frac{1}{2}}$—$e^3F_{2\frac{1}{2}}$		
54. 74	40		44. 92	$a^2F_{2\frac{1}{2}}$—$y^3F^0_{3\frac{1}{2}}$		
43. 38	2		55. 95	$y^2P^0_{1\frac{1}{2}}$—$e^4F_{1\frac{1}{2}}$		
41. 20	10		58. 06	$a^2F_{2\frac{1}{2}}$—$y^3F^0_{3\frac{1}{2}}$		
30. 82	5		68. 17			
10, 111. 9	2 h		9, 886. 6			
10, 083. 96	2		9, 914. 03			
66. 77	6		30. 95			
58. 79	2		34. 84			
54. 82	2		42. 76			
29. 74	2		67. 62			
14. 45	4		82. 84			
10, 005. 73	50		9, 991. 54			
9, 988. 47	10		10, 008. 80			
81. 24	6		016. 05	$y^4F^0_{3\frac{1}{2}}$—$e^4F_{2\frac{1}{2}}$		
80. 38	10		016. 91			
65. 70	3		031. 67			
32. 72	2		064. 98	$z^4D^0_{2\frac{1}{2}}$—31		
20. 82	150		077. 06	$a^4P_{1\frac{1}{2}}$—$z^4P_{1\frac{1}{2}}$		
9, 911. 08	3		085. 95			
9, 881. 24	100		117. 42	$a^4P_{2\frac{1}{2}}$—$z^4P^0_{1\frac{1}{2}}$		
62. 60	3		136. 54	$a^4F_{3\frac{1}{2}}$—$z^4F^0_{3\frac{1}{2}}$		
52. 58	6		146. 85	$z^2F^0_{2\frac{1}{2}}$—$e^2F_{2\frac{1}{2}}$		
48. 70	4		150. 84			
42. 0	2		157. 8			
33. 30	3 h		166. 74			
05. 2	1 h		195. 9	$b^3D_{2\frac{1}{2}}$—$y^3D^0_{3\frac{1}{2}}$		
9, 804. 20	2		196. 92			
9, 775. 09	8		227. 28			
72. 24	20		230. 26	$a^4P_{2\frac{1}{2}}$—$y^3F^0_{3\frac{1}{2}}$		
68. 82	3 h		233. 85			
37. 09	100		267. 20	$a^4P_{2\frac{1}{2}}$—$z^4G^0_{3\frac{1}{2}}$		
13. 52	3		292. 11			
09. 45	10		296. 42	$y^4F^0_{3\frac{1}{2}}$—$e^4F_{2\frac{1}{2}}$		
9, 706. 48	20		299. 57	$a^2P_{1\frac{1}{2}}$—$y^2P^0_{1\frac{1}{2}}$		
9, 699. 64	20		306. 84	$a^4P_{1\frac{1}{2}}$—$z^4P^0_{1\frac{1}{2}}$		
96. 7	1		310. 0			
92. 6	2		314. 3			

TABLE 6.—*The arc spectrum of lanthanum (La I)*—Continued

λ_{air} I. A.	Intensities, temperature class		ν_{vac} cm^{-1}	Term combination	Zeeman effects	
	B. S.	K. & C.			Observed	Computed
72.04	8		336.25	$a^4P_{1\frac{1}{2}}$—$z^4P^0_{0\frac{1}{2}}$		
46.47	3		363.65	$a^2P_{1\frac{1}{2}}$—$y^4F^0_{1\frac{1}{2}}$		
40.81	30		369.73			
33.72	40		377.36	$a^2G_{3\frac{1}{2}}$—$y^4F^0_{3\frac{1}{2}}$		
9, 631.84	2		379.38			
9, 570.38	5		446.04	$x^2F^0_{3\frac{1}{2}}$—$e^2F_{3\frac{1}{2}}$		
60.69	10		456.63	$a^4P_{1\frac{1}{2}}$—$z^4G^0_{2\frac{1}{2}}$		
42.06	50		477.05	$a^4P_{2\frac{1}{2}}$—$z^4P^0_{2\frac{1}{2}}$		
41.23	20		477.96	$a^2P_{1\frac{1}{2}}$—$y^2P^0_{0\frac{1}{2}}$		
9, 528.0	1 h		492.5	$a^4P_{2\frac{1}{2}}$—$y^2D^0_{1\frac{1}{2}}$		
9, 485.15	15		539.91	$y^4F^0_{1\frac{1}{2}}$—$e^4F_{0\frac{1}{2}}$		
84.2	1		541.0			
76.98	3		548.99	$z^4F^0_{1\frac{1}{2}}$—31		
74.45	5		551.81	$a^2F_{2\frac{1}{2}}$—$z^4G^0_{1\frac{1}{2}}$		
67.25	2		559.84			
61.82	60		565.89	$a^4P_{\frac{1}{2}}$—$z^4P^0_{1\frac{1}{2}}$		
57.62	2		570.59			
41.7	1		588.4			
38.30	100		592.23	$a^4F_{1\frac{1}{2}}$—$z^4F^0_{1\frac{1}{2}}$		
15.64	3		617.71			
9, 412.65	100		621.08	$a^4F_{2\frac{1}{2}}$—$z^4F^0_{2\frac{1}{2}}$		
9, 398.2	1		637.4			
90.56	4		646.07			
77.71	3		660.66	$z^2G^0_{3\frac{1}{2}}$—$e^2F_{3\frac{1}{2}}$		
76.10	3		662.49			
72.57	30		666.51	$a^4P_{1\frac{1}{2}}$—$z^4P^0_{1\frac{1}{2}}$		
28.87	2		716.47			
24.5	1		721.5	$y^4F^0_{2\frac{1}{2}}$—$e^4F_{2\frac{1}{2}}$		
9, 321.9	1 h		724.5	$y^4F^0_{1\frac{1}{2}}$—$e^2F_{2\frac{1}{2}}$		
9, 293.3	2 h		757.5			
87.5	1 h		764.2	$z^2D^0_{2\frac{1}{2}}$—31		
54.70	10		802.36	$a^2G_{3\frac{1}{2}}$—$y^4F^0_{3\frac{1}{2}}$		
50.06	20		807.78			
26.63	30		835.22	$b^2D_{2\frac{1}{2}}$—$y^2P^0_{1\frac{1}{2}}$		
9, 219.64	10		843.44	$a^2G_{4\frac{1}{2}}$—$y^4F^0_{3\frac{1}{2}}$		
9, 172.88	5		898.71			
72.39	10		899.30	$b^2D_{2\frac{1}{2}}$—$y^4F^0_{1\frac{1}{2}}$		
57.13	10		917.46			
51.62	6		924.03	$a^4P_{2\frac{1}{2}}$—$z^4G^0_{1\frac{1}{2}}$		
43.78	5		933.40	$b^2D_{1\frac{1}{2}}$—$y^2D^0_{1\frac{1}{2}}$		
42.24	6		935.24	$a^2D_{1\frac{1}{2}}$—$z^4G^0_{2\frac{1}{2}}$		
19.18	20		962.89	$a^4F_{1\frac{1}{2}}$—$z^4F^0_{2\frac{1}{2}}$		
9, 109.25	2		10, 974.84	$a^2P_{\frac{1}{2}}$—$y^2P^0_{\frac{1}{2}}$		
9, 079.10	50		11, 011.29	$a^2G_{3\frac{1}{2}}$—$z^2F^0_{3\frac{1}{2}}$		
58.63	2		036.17	$y^4F^0_{1\frac{1}{2}}$—$e^2F_{2\frac{1}{2}}$		
56.53	5		038.73	$a^2P_{1\frac{1}{2}}$—$y^4F^0_{1\frac{1}{2}}$		
46.97	2		050.39			
25.05	4		077.23	$a^2F_{2\frac{1}{2}}$—$z^4G^0_{1\frac{1}{2}}$		
9, 008.26	6		097.88			
8, 977.39	2		136.04	$x^2F^0_{2\frac{1}{2}}$—$e^2F_{2\frac{1}{2}}$		
70.07	3		145.13	$a^2F_{2\frac{1}{2}}$—$z^4P^0_{2\frac{1}{2}}$		
65.41	2		150.92			
63.63	10		153.13	$a^2P_{1\frac{1}{2}}$—$y^2P^0_{0\frac{1}{2}}$		
57.74	50		160.47	$a^2F_{2\frac{1}{2}}$—$y^2D^0_{1\frac{1}{2}}$		
48.89	2		171.50			
47.95	1		172.68			
8, 917.70	1 h		210.58			
8, 891.06	1		244.17			
84.24	2		252.80	$a^2P_{1\frac{1}{2}}$—$x^2F^0_{2\frac{1}{2}}$		
79.56	3		258.73			
75.05	2		264.45			
71.00	4		269.60			
67.35	3		274.24			
39.64	20		309.57	$a^4F_{3\frac{1}{2}}$—$z^2D^0_{2\frac{1}{2}}$		
25.56	50		327.23	$a^2F_{2\frac{1}{2}}$—$y^2D^0_{1\frac{1}{2}}$		

TABLE 6.—*The arc spectrum of lanthanum (La I)*—Continued

λ air I. A.	Intensities, temperature class		ν vac cm⁻¹	Term combination	Zeeman effects	
	B. S.	K. & C.			Observed	Computed
21.66	1 h		332.62			
8,818.96	20		336.10			
8,797.6	2 h		363.6			
72.02	1		396.76			
67.92	4		402.07			
60.4	1		411.9			
48.42	50		427.50	$a^4F_{1\frac{1}{2}}-z^4D^0_{1\frac{1}{2}}$		
24.12	1		459.33			
20.42	20		464.19	$a^3G_{4\frac{1}{2}}-y^4P^1_{2\frac{1}{2}}$		
8,703.13	5		486.97	$a^3G_{3\frac{1}{2}}-z^3G^1_{3\frac{1}{2}}$		
8,674.40	60		525.01	$a^4F_{3\frac{1}{2}}-z^4F^1_{3\frac{1}{2}}$		
72.10	30		528.07	$a^3G_{4\frac{1}{2}}-z^3G^1_{4\frac{1}{2}}$		
38.4	10		573.0	$b^2D_{1\frac{1}{2}}-y^2P^1_{1\frac{1}{2}}$		
24.22	6		592.07	$a^3F_{3\frac{1}{2}}-z^3G^1_{3\frac{1}{2}}$		
8,621.55	2		595.66			
8,590.97	6		636.94	$b^2D_{1\frac{1}{2}}-y^4F^1_{1\frac{1}{2}}$		
58.9	1		680.5	$y^2D^0_{1\frac{1}{2}}-e^4F^1_{1\frac{1}{2}}$		
45.44	50		698.94	$a^4F_{1\frac{1}{2}}-z^4D^1_{1\frac{1}{2}}$		
43.46	20		701.65	$a^3G_{3\frac{1}{2}}-z^2F^1_{2\frac{1}{2}}$		
29.68	3		720.55			
13.55	15		742.76	$a^3G_{4\frac{1}{2}}-z^3F^1_{3\frac{1}{2}}$		
8,507.37	10		751.29	$b^2D_{1\frac{1}{2}}-y^2P^0_{0\frac{1}{2}}$		
8,476.48	30		794.12	$a^4F_{2\frac{1}{2}}-z^3D^1_{2\frac{1}{2}}$		
67.62	15		806.45	$z^4G^0_{5\frac{1}{2}}-e^4F^1_{4\frac{1}{2}}$		
8,440.06	3		845.01			
8,379.80	20		930.18	$z^4G^0_{4\frac{1}{2}}-e^4F^1_{3\frac{1}{2}}$		
58.50	2 h		960.59			
46.60	100	12, III	977.64	$a^4F_{4\frac{1}{2}}-z^4D^1_{3\frac{1}{2}}$		
34.44	3		11,995.11			
24.72	100	15, III	12,009.12	$a^4F_{3\frac{1}{2}}-z^4D^1_{2\frac{1}{2}}$		
24.59	HNR	1, III A	009.30	$a^4F_{2\frac{1}{2}}-z^4F^1_{2\frac{1}{2}}$		
16.05	10	2, IV A	021.64	$a^4F_{2\frac{1}{2}}-z^2D^1_{1\frac{1}{2}}$		
8,302.82	4		040.80	$a^4F_{1\frac{1}{2}}-z^4D^1_{1\frac{1}{2}}$		
8,247.46	60	10, III	121.62	$a^4F_{4\frac{1}{2}}-z^4F^1_{4\frac{1}{2}}$		
37.90	3		135.68	$a^4F_{1\frac{1}{2}}-z^2D^1_{1\frac{1}{2}}$		
11.65	2		174.48			
8,203.38	3		186.75	$a^4F_{2\frac{1}{2}}-z^2F^1_{2\frac{1}{2}}$		
8,086.10	20+M	15, III	363.50	$a^4F_{1\frac{1}{2}}-z^2D^1_{1\frac{1}{2}}$		
84.53	3		365.92	$a^2G_{4\frac{1}{2}}-z^2G^1_{4\frac{1}{2}}$		
51.38	10	10, III	416.82	$a^4F_{4\frac{1}{2}}-z^2F^1_{3\frac{1}{2}}$		
8,001.91	4	4, III A	493.58	$a^4F_{2\frac{1}{2}}-z^4D^1_{2\frac{1}{2}}$		
7,964.86	5	6, III	551.70	$a^4F_{1\frac{1}{2}}-z^2P^0_{1\frac{1}{2}}$		
48.30	HNR	10, III	577.85	$a^2D_{2\frac{1}{2}}-z^4F^1_{2\frac{1}{2}}$		
7,931.18	1		605.00	$a^4F_{2\frac{1}{2}}-z^4D^1_{1\frac{1}{2}}$		
7,864.98	1		711.10	$a^2F_{2\frac{1}{2}}-y^4F^1_{2\frac{1}{2}}$		
7,841.76	3		748.74	$a^4F_{2\frac{1}{2}}-z^4F^1_{1\frac{1}{2}}$		
7,737.74	1 h		12,920.12	$a^2F_{2\frac{1}{2}}-z^2F^1_{2\frac{1}{2}}$		
7,664.38	4	? III	13,043.78	$a^4F_{3\frac{1}{2}}-z^2F^1_{3\frac{1}{2}}$		
7,539.24	10	15, II	260.29	$a^2D_{1\frac{1}{2}}-z^4F^1_{1\frac{1}{2}}$		
33.64	2		270.14	$a^4F_{2\frac{1}{2}}-z^2P^1_{1\frac{1}{2}}$		
7,501.78	1		326.50	$a^2F_{2\frac{1}{2}}-y^4F^1_{2\frac{1}{2}}$		
7,498.82	2	5, III A	331.76	$a^2F_{2\frac{1}{2}}-y^4F^1_{1\frac{1}{2}}$		
7,463.08	5	10, III	395.61	$a^2F_{2\frac{1}{2}}-z^2G^1_{3\frac{1}{2}}$		
7,382.73	6	5, III A	541.40	$a^2P_{1\frac{1}{2}}-z^2S^0_{\frac{1}{2}}$		
79.71		10, III A	546.94	$a^2G_{4\frac{1}{2}}-y^2G^1_{4\frac{1}{2}}$		
45.36	25	20, III A	610.30	$a^2F_{2\frac{1}{2}}-z^2F^1_{2\frac{1}{2}}$	(0.42) 1.18 ?	(0.39) 1.06
44.42	HNR	2, III A	612.03	$a^4F_{1\frac{1}{2}}-z^2P^1_{1\frac{1}{2}}$		
34.18	50	60, II	631.04	$a^2D_{1\frac{1}{2}}-z^4F^1_{1\frac{1}{2}}$	(0.00w) 1.30 w	(0.00) 1.30
20.90	2		655.77	$a^2D_{2\frac{1}{2}}-z^4D^1_{2\frac{1}{2}}$		
7,308.46	2 h		679.01	$a^2S_{\frac{1}{2}}-{}^4S^1_{\frac{1}{2}}$		
7,285.83	1		721.50			
70.30	HNR	5, II A	750.81	$a^2D_{2\frac{1}{2}}-z^2D^1_{2\frac{1}{2}}$		
70.07	HNR	10, III	751.24	$a^2F_{3\frac{1}{2}}-y^4F^1_{3\frac{1}{2}}$		
63.68	2		763.34			
62.83	2		764.95			

TABLE 6.—*The arc spectrum of lanthanum (La I)*—Continued

λ air I. A.	Intensities, temperature class		ν vac. cm^{-1}	Term combination	Zeeman effects	
	B. S.	K. & C.			Observed	Computed
50.38	1		788.59	$a^4F_{4½}—y^2F^0_{5½}$		
19.92	15	15, II A	846.76	$a^4F_{2½}—y^2F^0_{3½}$		
7,217.16	2		852.06			
7,161.25	40	50, III	960.20	$a^2F_{2½}—x^2F^0_{3½}$	(0.00) 0.91	(0.00) 0.90
58.11	30	50, III A	966.32	$a^2D_{2½}—z^4F^0_{3½}$	(0.00) 1.27	(0.00) 1.22
51.92	HNR	1, III A	978.42	$a^2D2_{½}—z^2D^0_{1½}$		
7,149.76	2	2, III	13,982.63	$a^4P_{2½}—x^2F^0_{3½}$		
7,098.18	2		14,084.24			
92.40	HNR	2, I A	095.72	$a^2D_{1½}—z^4D^0_{1½}$		
76.36	3	3, III	127.67			
68.37	60	100, II	143.64	$a^2D_{2½}—z^2F^0_{2½}$	(0.69)?	(0.66) 1.05
62.4	1 h		155.6	$a^2P_{1½}—w^2F^0_{2½}$		
45.96	200	300, II	188.62	$a^4F_{1½}—y^2F^0_{2½}$	(0.21, 0.65) 1.04, 1.47	(0.21, 0.62) 0.20, 0.63 1.04, 1.46
32.07	25	15, III	216.65	$a^3P_{½}—z^3S^0_{1½}$	(0.60) 1.27	(0.60) 1.27
23.67	150	150, III	233.66	$a^2F_{3½}—z^2G^0_{4½}$	(0.00) 1.16	(0.00) 1.16
7,013.15	2		255.00	$z^4D^0_{3½}—e^4F_{2½}$		
6,978.09	2		326.62	$a^2P_{1½}—z^4D^0_{2½}$		
76.87	2	3, III	329.13			
35.03	50	50, III	415.58	$a^4F_{3½}—y^2F^0_{3½}$	(0.48) 1.14	(0.41) 1.15
25.27	80	100, III	435.90	$a^2F_{2½}—z^2G^0_{3½}$	(0.00w) 1.58 A[3]	(0.00) 1.53 A[3]
18.33	8	8, III A	450.38	$a^2D_{2½}—z^4D^0_{3½}$		
17.26	10	10, III A	452.61	$a^4F_{3½}—z^4G^0_{3½}$		
03.08	2	1, III A	482.30	$a^4F_{4½}—z^4G^0_{3½}$		
6,902.08	3	1, III	484.40	$a^2P_{½}—z^4D^0_{½}$		
6,889.63	2 h	tr, V	489.54	$a^2G_{4½}—w^2F^0_{3½}$		
98.41		tr, V	492.10			
23.80	40	15, II A	650.56	$a^2F_{2½}—z^2F^0_{3½}$	(0.00) 1.15	(0.00) 1.12
21.51	5 d	3n, V	655.47			
19.14	1		660.57	$a^2P_{½}—z^4D^0_{1½}$		
6,816.29		1n, V?	666.70			
6,796.73	4	4, II A	708.90	$a^2D1_{½}—z^4D^0_{1½}$		
83.55	1	tr, IV A	737.48			
78.19	1	tr, V	749.14	$z^2F^0_{3½}—e^4D_{3½}$		
76.69	1	1, III A	752.40	$z^4O_{1½}—33$		
60.73	HNR	1, III A	787.23	$a^4F_{2½}—z^4P^0_{1½}$		
60.23	1		788.32	$a^2P_{1½}—y^2P^0_{2½}$		
53.05	40	50, I A	804.04	$a^2D_{1½}—z^2D^0_{2½}$	(0.00 w) 1.51 A[3]	(0.00) 1.51 A[3]
48.12	10	10, II A	814.86	$b^2D_{1½}—z^2S^0_{½}$		
41.20	2		830.07			
37.29	1		838.67			
15.96		1, IVA?	885.80	$z^4D^0_{1½}—34$		
6,709.49	150	200, I	900.16	$a^4F_{3½}—y^2F^0_{3½}$	(0.00) 1.18	(0.00) 1.14
6,699.86	3	4, III A	921.57			
99.26	2	2, III?	922.91			
92.86	20	30, I A	14,937.18	$a^4F_{2½}—z^4G^0_{2½}$	(0.00) 1.06	(0.09) 1.05
64.45	1		15,000.85			
61.40	60	80, I A	007.72	$a^4F_{4½}—z^4G^0_{4½}$	(0.65) 1.23 B?	(0.66) 1.24
58.06	1		015.25	$a^4P_{½}—y^4D^0_{½}$		
50.81	80	100, I A	031.62	$a^2D_{1½}—z^4D^0_{1½}$	(0.00 w) 0.88	(0.25) 0.88
45.15	7	8, IV	044.42	$z^4F^0_{4½}—e^4D_{3½}$		
44.40	30	40, I A	046.12	$a^2D_{2½}—z^4D^0_{2½}$		
31.20	3	3, V?	076.07			
28.4	1	1, IV A	082.4	$b^2D_{1½}—x^4D^0_{½}$		
16.59	60	80, I	109.36	$a^4F_{3½}—z^4G^0_{3½}$	(0.50) 1.12 B	(0.47) 1.14
12.48	3		118.75			
08.25	40	40, II	128.43	$a^2G_{3½}—z^2H^0_{4½}$	(0.00) 1.01	(0.00) 1.00
07.7	1	3, IV	129.7	$a^2P_{½}—4f_{1½}$		
6,600.17	25	50, II A	146.95	$a^4F_{2½}—z^4P^0_{2½}$	(0.35) 1.12	(0.37) 1.12
6,599.48		tr, IV A	148.53			
93.45	40	60, I	162.39	$a^4F_{3½}—y^2D^0_{2½}$	(0.00 w) 1.30 A[3]	(0.00) 1.33 A[3]
90.59	1		168.97	$a^2F_{3½}—1f_{3½}$		
82.18	4	6, IV	188.35	$z^4D^0_{3½}—e^4D_{3½}$	(0.00 h) 1.41	
78.51	200	400, I	196.82	$a^2D_{1½}—z^2F^0_{2½}$	(0.00) 1.00	(0.00) 0.98
68.54	1		219.89	$a^2D_{1½}—z^2P^0_{½}$		
65.45	40	40, I A	227.05	$a^2D_{2½}—z^2P^0_{1½}$		

TABLE 6.—*The arc spectrum of lanthanum (La I)*—Continued

λ_{air} I. A.	Intensities, temperature class		ν_{vac} cm^{-1}	Term combination	Zeeman effects	
	B. S.	K. & C.			Observed	Computed
55.95		3, III A	249.12			
55.11	2	1, V	251.07	$a^2F_{3½}$—$y^4D_{3½}$		
51.78	1		258.82	$b^2D_{1½}$—$z^4D^1_{½}$		
49.16	2	2 n, III?	264.92	$a^2P_{1½}$—$z^4F^1_{½}$		
43.17	300	500, I	278.90	$a^4F_{1½}$—$z^4G^1_{½}$	(0, 33, 0.99) 0.00, 0.74, 1.41, 2.07	(0, 33, 0.99) 0.08, 0.75, 1.40, 2.06
23.86	2	2, III A?	324.12	$b^2D_{2½}$—$e^2F^1_{½}$		
20.70	15	20, IV	331.55		(0.00 h) 1.10 h	
19.30	3	4, IV	334.84	$z^4F^1_{½}$—$e^4F_{2½}$		
17.35	1		339.43	$z^4G^1_{½}$—35		
6,506.25	4	6, IV	365.59	$z^4D^1_{½}$—33		
6,492.86	4	5, V	397.29			
85.54	20	20, II A	414.66	$a^2F_{3½}$—$2^1_{½}$	(0.00) 1.10	(0.00) 1.10
80.20	1		427.37	$a^2F_{2½}$—$y^4D^1_{½}$		
68.44	10	8, II A	455.42	$b^2D_{2½}$—$z^4S^1_{½}$		
55.99	250	300, I	485.22	$a^2D_{2½}$—$z^2F^1_{½}$	(0.00) 1.18	(0.00) 1.15
54.50	150	200, I	488.80	$a^4F_{1½}$—$z^4P^1_{½}$	(0.38, 1.11) 0.80, 1.54, 2.26	(0.39, 1.18) 0.02, 0.81, 159, 2.38
50.34	6	8, II A	498.78	$a^2P_{1½}$—$z^2D^1_{½}$	(0.00) 1.29	(0.00) 1.20
49.94	3		499.74			
48.25	4	10?, II A	503.81	$a^2D_{1½}$—$z^4D^1_{½}$		
48.10	20	50?, II A	504.17	$a^4F_{1½}$—$y^2D^1_{½}$		
26.60	2		556.04	$z^4D^1_{½}$—$e^4F_{2½}$		
20.90	1		569.85	$z^2F^1_{½}$—$e^2F_{2½}$		
17.23	2	3, III? A	578.85	$b^2D_{2½}$—$z^2D^1_{½}$		
6,410.98	200	300, I	593.94	$a^4F_{2½}$—$z^4G^1_{½}$	(0.00) 1.09	(0.00) 1.10
6,394.23	400	600, I	634.79	$a^4F_{3½}$—$z^4G^1_{½}$	(0.00 W) 1.02 A[1]	(0.00) 0.90 A[1]
80.48	1	1, V	668.48			
75.50	2		680.72	$z^4F^1_{4½}$—$e^4F_{4½}$		
75.11	2	2, V	681.68			
60.20	30	30, II	718.44	$a^2P_{½}$—$z^2D^1_{1½}$	(0.00) 0.89	(0.00) 0.93
56.38	3	4, III A	727.88	$b^2D_{1½}$—$L^1_{1½}$		
53.63	1		734.69	$a^2P_{1½}$—$z^2P^1_{½}$		
39.16	2	2, III A	770.61	$a^4P_{1½}$—$z^2S^1_{½}$		
33.74	3	2, IV?	784.10	$z^4D^1_{½}$—$e^4D_{1½}$		
33.24	2	2, III?	785.35			
30.42	3	2, III A	792.38	$a^2F_{2½}$—$y^4D^1_{2½}$		
25.90	100	150, I	803.67	$a^2D_{2½}$—$y^2F^1_{½}$	(0.63, 0.99) 0.25, 0.63, 1.01, 1.38, 1.76	(0.19, 0.56, 0.94) 0.27, 0.64, 1.01, 1.39, 1.77
18.26	5	12, III A	822.78	$a^2F_{3½}$—$w^2F^1_{3½}$		
10.13	8	12, IV	843.16			
08.87	2	2, III	846.32			
6,308.21	2	3, III	847.98			
6,293.57	60	80, II A	884.85	$a^4F_{3½}$—$y^2D^1_{2½}$	(0.00) 1.33	(0.00) 1.26
88.56	6	7, III A	897.50	$a^2P_{1½}$—$y^4P^1_{½}$		
87.73	7	8, III A	899.60	$b^2D_{2½}$—$z^4D^1_{½}$		
78.31	1		923.46	$a^2P_{1½}$—$y^4P^1_{½}$		
66.00	40	60, III	954.74	$a^2G_{4½}$—$z^2H^1_{5½}$	(0.00) 1.06	(0.00) 1.06
49.92	300	500, I	15,995.79	$a^4F_{4½}$—$z^4G^1_{5½}$	(0.00) 1.13	(0.00) 1.14
38.58	12	15, III A	16,024.86	$a^4P_{2½}$—$z^4D^1_{2½}$		
36.76	7	10, III A	029.54	$a^4P_{½}$—$z^2S^1_{½}$		
36.17	8	12, IV	031.06			
34.85	10	15, III A	034.45	$b^2D_{2½}$—$z^2D^1_{2½}$	(0.00) 1.26	(0.09) 1.27
33.51	10	15, III A	037.90	$a^4P_{1½}$—$z^4D^1_{½}$		
32.56	1		040.34	$z^4F^1_{½}$—$e^4F_{3½}$		
25.33	2 h		058.97	$a^4P_{1½}$—$3^1_{½}$		
24.24	1		061.78	$b^2D_{1½}$—$e^2F^1_{½}$		
19.46	2	2, V	074.13			
18.19	5	7, III	077.41	$a^2G_{4½}$—$z^4F^1_{4½}$		
14.35	2		087.34	$z^2D^1_{½}$—$e^2F_{2½}$		
6,206.76	2		107.02			
6,173.74		1, IV A	193.17	$b^2D_{1½}$—$z^4S^1_{½}$		
67.69	2		209.05	$a^2F_{2½}$—$1^1_{2½}$		

TABLE 6.—*The arc spectrum of lanthanum (La I)*—Continued

λ_{air} I. A.	Intensities, temperature class		ν_{vac} cm^{-1}	Term combination	Zeeman effects	
	B. S.	K. & C.			Observed	Computed
65.69	30	40, II	214.31	$a^4P_{1\frac{1}{2}}-x^4D^1_{1\frac{1}{2}}$	(0.88) 0.87, **1.43**, 1.99	(0.27, **0.81**) 0.88, **1.42**, 1.96
65.02	3	2, IV	216.07			
54.55	1		243.66	$z^4F^1_{3\frac{1}{2}}-e^4F_{1\frac{1}{2}}$		
46.53	10	5, IV	264.85	$a^2S_{\frac{1}{2}}-{}^3P_{1\frac{1}{2}}$		
45.29	3	3, III	268.13	$z^4F^1_{3\frac{1}{2}}-e^4D_{3\frac{1}{2}}$		
42.98	10	10, III	274.25		(0.00) 1.15	
41.71	3		277.61			
36.48	2	2, II A	291.49	$a^2F_{3\frac{1}{2}}-y^4D^1_{3\frac{1}{2}}$		
34.39	20	30, III	297.04	$a^4P_{\frac{1}{2}}-x^4D^1_{\frac{1}{2}}$	(1.34) 1.37	(1.35) 1.35
27.04	8	12, III A	316.59	$b^2D_{1\frac{1}{2}}-x^2D^1_{1\frac{1}{2}}$		
23.75	2	2, IV	325.36			
21.27		1, IV	331.97			
20.34		1, IV	334.45	$z^4F_{1\frac{1}{2}}-34$		
11.71	20	30, II	357.52	$a^2F_{3\frac{1}{2}}-w^2F_{3\frac{1}{2}}$	(0.00) 1.17	(0.12) 1.15
08.47	40	60, II	366.19	$a^4P_{2\frac{1}{2}}-x^4D^1_{2\frac{1}{2}}$	(0.53) 1.34B	(−, 0.48, **0.80**) −, 1.06, **1.38**, 1.70, −
6,107.26	4	12, II A	369.43	$a^4F_{3\frac{1}{2}}-y^2D^1_{2\frac{1}{2}}$		
6,092.22	2	1, III A	409.85	$a^2P_{1\frac{1}{2}}-x^2P^0_{0\frac{1}{2}}$ $z^4D^1_{1\frac{1}{2}}-e^2F_{2\frac{1}{2}}$		
88.06	2	1n, IV	421.22			
84.86	5	8, III	429.69	$y^2F^1_{2\frac{1}{2}}-35$		
75.24		1, III A	455.71	$a^2F_{2\frac{1}{2}}-v^2F^1_{2\frac{1}{2}}$		
74.01	3	1, III A	459.04	$b^2D_{2\frac{1}{2}}-y^4P^1_{1\frac{1}{2}}$		
72.04	3	4, III A	464.38	$b^2D_{1\frac{1}{2}}-z^4F^1_{1\frac{1}{2}}$		
68.70	20	30, III	473.44	$a^4P_{\frac{1}{2}}-x^4D^1_{\frac{1}{2}}$	(0.75) **0.40**, 1.90	(0.77) **0.38**, 1.93
44.8	2	2, III A	538.6	$b^2D_{1\frac{1}{2}}-x^4F^1_{1\frac{1}{2}}$		
41.6	2	2, III	547.3			
38.57	20	25, III A	555.64	$a^4P_{1\frac{1}{2}}-x^4D^1_{2\frac{1}{2}}$		
34.5	2 h	3, V	566.8			
32.38	5		572.63	$a^2P_{\frac{1}{2}}-y^4P^0_{1\frac{1}{2}}$		
31.46	5	3n, IV?	575.15			
25.09	2 p?	1, IV?	592.68			
17.16	3	1, III A	614.54	$z^4F^1_{1\frac{1}{2}}-e^4F_{1\frac{1}{2}}$		
6,007.34	50	50, III A	641.70	$a^4F_{4\frac{1}{2}}-y^4F^1_{3\frac{1}{2}}$	(0.00 w) 1.77 A^3	(0.00) 1.85 A^3
5,992.35	3	2, III A	683.33	$a^4P_{1\frac{1}{2}}-4^1_{1\frac{1}{2}}$		
82.34	10	5, III A	711.25	$a^4F_{1\frac{1}{2}}-y^2D^1_{2\frac{1}{2}}$		
75.75	10	3, III A	729.68	$a^4F_{2\frac{1}{2}}-w^2F^1_{2\frac{1}{2}}$		
70.58	HNR	1, III A	744.16	$a^2D_{2\frac{1}{2}}-z^4P^1_{1\frac{1}{2}}$		
62.30	3	1, III	758.98			
62.59	4	1, III A	766.60	$b^2D_{2\frac{1}{2}}-x^2P^1_{1\frac{1}{2}}$		
60.59	4	3, III A	772.23	$b^2D_{1\frac{1}{2}}-x^2D^1_{2\frac{1}{2}}$		
40.83	3	1, III A	828.01	$a^4P_{2\frac{1}{2}}-v^2F^1_{2\frac{1}{2}}$		
35.29	20	15, II A	843.72	$a^4F_{3\frac{1}{2}}-y^4F^1_{3\frac{1}{2}}$	(0.00 w) 1.72 A^3	(0.00) 1.76 A^3
30.68	100	400, I	856.81	$a^2D_{1\frac{1}{2}}-y^2F^1_{2\frac{1}{2}}$		(0.00) 0.86
30.61	200		857.01	$a^2D_{2\frac{1}{2}}-y^2F^1_{3\frac{1}{2}}$	(0.00) 0.87	(0.26) 1.14
28.48	5	4, III A	863.07	$a^2F_{3\frac{1}{2}}-w^2F^1_{3\frac{1}{2}}$		
17.64	20	15, II A	893.96	$a^2D_{2\frac{1}{2}}-z^4G^1_{3\frac{1}{2}}$	(0.27) 1.10 h	(0.29) 1.13
04.28	4	2, III A	932.20	$a^2F_{3\frac{1}{2}}-x^4F^1_{3\frac{1}{2}}$	(0.00) 1.25	(0.00) 1.16
5,900.75	3	1, III A	942.31	$a^4P_{\frac{1}{2}}-4^1_{\frac{1}{2}}$		
5,894.84	20	8, III A	16,959.30	$a^4P_{2\frac{1}{2}}-z^4S^1_{1\frac{1}{2}}$		
77.96	3	1, III A	17,008.00	$a^2S_{\frac{1}{2}}-w^2D^1_{1\frac{1}{2}}$		
77.62	4	2, III A	008.98	$a^4F_{2\frac{1}{2}}-y^2P^1_{1\frac{1}{2}}$		
74.72	8	8, III A	017.38	$a^4P_{1\frac{1}{2}}-e^2F^1_{2\frac{1}{2}}$		
69.93	2	1, III A	031.27	$a^2F_{3\frac{1}{2}}-x^4D^1_{3\frac{1}{2}}$		
57.44	2		067.58			
55.57	20	15, II A	073.03	$a^4F_{2\frac{1}{2}}-y^4F^1_{1\frac{1}{2}}$	(0.00 w) 1.42 A^3	(0.00) 1.41 A^3
52.26	6	2, III A	082.69	$a^4P_{2\frac{1}{2}}-x^2D^1_{2\frac{1}{2}}$		
48.37	15	8, III A	094.05	$z^4F^1_{1\frac{1}{2}}-e^4F_{2\frac{1}{2}}$	(0.00) 0.90	
45.02	10	6, III A	103.85	$a^2D_{2\frac{1}{2}}-z^4P^1_{1\frac{1}{2}}$	(0.00) 1.18	(0.00) 1.20
39.77	3	2, II A	119.23	$a^2D_{2\frac{1}{2}}-y^2D^1_{2\frac{1}{2}}$		
29.71	20	10, III A	148.77	$a^4P_{1\frac{1}{2}}-z^4S^1_{1\frac{1}{2}}$	(0.00) 1.75	(0.17) 1.75
27.56	8	3, III A	155.10	$b^2D_{2\frac{1}{2}}-y^4P^1_{2\frac{1}{2}}$	(0.59) 1.50 ?	(0.55) 1.42

TABLE 6.—*The arc spectrum of lanthanum (La I)*—Continued

λ air I. A.	Intensities, temperature class		ν vac cm⁻¹	Term combination	Zeeman effects	
	B. S.	K. & C.			Observed	Computed
23.82	15	10, III A	166.11	$a^3F_{3½}-z^2D^0_{2½}$	(0.00 w) 0.96 h	(0.00) 0.98
21.98	30	30, III	171.54	$a^3G_{3½}-y^2G^0_{4½}$	(0.00) 0.93	(0.12) 0.93
13.44	2	1, III A	196.76	$b^3D_{1½}-y^4P^0_{½}$		
5,802.10	2	1, III A	230.37	$a^4P^0_{2½}-x^4F^0_{1½}$		
5,791.32	200	400, I	262.45	$a^4F_{4½}-y^4F^0_{4½}$	(0.00 w) 1.31 B	(0.18) 1.30
89.22	150	250, I	268.71	$a^4F_{3½}-y^4F^0_{3½}$	(0.15) 1.21	(0.12) 1.20
69.97	25	25, III A	326.32	$a^3F_{3½}-v^3F^0_{3½}$		
69.32	80	80, I	328.27	$a^4F_{3½}-y^4F^0_{2½}$	(0.00) 1.01	(0.04) 1.02
61.83	50	60, I	350.80	$a^4F_{1½}-y^2P^0_{1½}$	(0.94) **0.00**, 0.68, 1.34	(0.32, **0.96**) 0.09, 0.73, 1.37
44.41	60	80, III	403.41	$a^4P^0_{2½}-x^4D^0_{3½}$	(0.00 w) 1.24	(0.00) 1.25
42.93	4	2, III A	407.90	$b^4P_{½}-z^4S^0_{1½}$		
40.65	80	100, I	414.81	$a^4F_{1½}-y^4F^0_{1½}$	(0.47) 0.59 B	(0.18, **0.55**) 0.33, 0.60, 0.96
34.93	6	5, III A	432.18	$a^3G_{3½}-u^3F^0_{2½}$	(0.00) 0.92	(0.00) 0.92
20.01	10	10, III A	477.65	$a^4F_{3½}-x^2F^0_{2½}$	(**0.16**, 0.48, 0.81) 1.93 A[2]	(**0.16**, 0.48, 0.80) 1.70, **2.03**
14.55		1, III A	494.35	$a^3G_{3½}-y^4G^0_{3½}$		
14.01	4	5, III A	496.00	$a^3F_{3½}-z^3F^0_{3½}$	(0.62) ?	(0.66) 1.05
10.85	2 p?	2, III	505.68	$a^3P_{1½}-w^3P^0_{1½}$		
03.32	20	10, III	528.80	$a^4F_{1½}-y^3F^0_{1½}$		
02.57		2, III	531.10	$a^4P_{1½}-x^2D^0_{1½}$		
5,701.15		1, III	535.47	$a^2G_{4½}-y^4G^0_{3½}$		
5,699.32	3	5, III	541.10	$a^4F_{4½}-z^2F^0_{3½}$		
96.18	30	40, I	550.77	$a^2D_{2½}-z^4G^0_{3½}$	(0.00 w) 0.80 A[1]	(0.00) 0.70 A[1]
61.34	2	1, III A	658.78	$a^3G_{3½}-y^3G^0_{4½}$		
57.71	30	50, II	670.10	$a^4F_{1½}-y^4F^0_{2½}$	(**0.29**, 0.88) 0.73, 1.33, **1.94**	(**0.29**, 0.89) 0.12, 0.71, **1.30**, **1.90**
56.54	2	1, III A	673.76	$a^2P_{1½}-u^2F^0_{2½}$		
54.8	20	3, III A	679.2	$a^4P_{½}-x^4F^0_{1½}$		
48.24	50	80, III	699.73	$a^2G_{4½}-y^2G^0_{4½}$	(0.00) 1.12	(0.00) 1.12
39.31	8	5, III A	727.76	$a^4P_{1½}-x^2D^0_{2½}$		
32.02	15	25, II	750.70	$a^2F_{2½}-x^4D^0_{1½}$	(0.00) 0.93	(0.00) 0.92
5,631.22	60	100, I	753.22	$a^4F_{2½}-y^4F^0_{3½}$	(0.00 W) 1.45 A[1]	(0.00) 1.55 A[2]
5,598.52	3		856.92		(0.00) 0.49	
88.33	100	20, II	889.48	$a^4F_{3½}-y^4F^0_{4½}$		
70.37	3	5, II A	947.16	$a^2D_{1½}-z^4G^0_{2½}$		
68.45	30	50, II	953.35	$a^4F_{2½}-z^2G^0_{3½}$	(0.44) 1.16	(0.41) 1.15
65.70	10	20, II	962.22	$a^4F_{2½}-x^2F^0_{2½}$		
65.43	10	20, III	963.09	$a^4P_{2½}-y^4P^0_{1½}$	(0.00) 1.52	(0.00) 1.49
62.54	2	2, III	17,972.42	$a^2F_{2½}-z^4F^0_{1½}$		
44.90	3	6, III	18,029.60	$a^2P_{1½}-Sf^0_{1½}$	(0.28) 1.47	(0.35) 1.44
41.25	15	20, III	041.47	$b^2D_{2½}-w^2P^0_{1½}$	(0.00) 1.25	(0.00) 1.25
32.17	4	3, III	071.08	$a^2F_{2½}-x^4D^0_{3½}$		
29.86	2	3, III	078.63	$a^2G_{3½}-u^2F^0_{3½}$		
26.51		1, V	089.59	$z^2F^0_{2½}-35$		
17.34	20	30, III	119.66	$a^2G_{4½}-u^2F^0_{3½}$	(0.00) 1.10	(0.00) 1.10
15.28	5	10, III	126.42	$a^4P_{1½}-y^4P^0_{½}$	(0.25) 1.42	(0.30) **1.39**, 2.00
07.33		2, III	152.59	$a^4P_{1½}-y^4P^0_{1½}$		
06.00	20	40, II	156.97	$a^2D_{1½}-z^4P^0_{2½}$	(0.00 w) 1.54 h	(0.00) 1.50
03.80	40	80, III	164.23	$a^4F_{4½}-z^2G^0_{3½}$	(0.70) 1.22 B	(0.69) 1.23
02.66	5	10, III	168.00	$a^4F_{3½}-z^2F^0_{3½}$		
02.24	3	4, III	169.38	$a^3G_{4½}-y^4G^0_{4½}$		
5,510.34	200	300, I	172.35	$a^2D_{1½}-y^2D^0_{1½}$	(0.00) 0.80	(0.06) 0.81
5,498.70	2	2n, III	181.08	$a^2P_{½}-w^2P^0_{1½}$		
91.07	5	8, III	206.34	$a^2F_{2½}-x^2D^0_{2½}$		
75.17	10	15, III	259.21		(0.00) 1.08	
66.91	2	3, III	286.80	$a^2F_{3½}-y^4P^0_{2½}$		
55.14	200	400, I	326.25	$a^2D_{2½}-y^2D^0_{1½}$	(0.00) 1.20	(0.02) 1.20
37.55	2	5, III	385.54	$a^4P_{½}-y^4P^0_{½}$	(0.00) 2.54	(0.21) 2.50
29.86	6	15, III	411.57	$a^4P_{½}-y^4P^0_{1½}$	(0.49) 1.04	(0.55) **1.06**, 2.15
22.10		3, III A	437.93	$a^4F_{3½}-z^2G^0_{3½}$		
5,415.67	4	8, III	459.82	$a^4P_{1½}-x^4P^0_{1½}$	(0.36) 1.56 w	(0.39) 1.56
5,390.63	?		545.56	$a^2G_{3½}-w^2D^0_{2½}$		

TABLE 6.—*The arc spectrum of lanthanum (La I)*—Continued

λ_{air} I. A.	Intensities, temperature class		ν_{vac} cm^{-1}	Term combination	Zeeman effects	
	B. S.	K. & C.			Observed	Computed
80.00	3	5, III	582.21	$a^2G_{3½}$—$t^2F^0_{3½}$		
65.87	4	8, III	631.14	$a^2F_{2½}$—$y^4P^0_{1½}$		
59.70	2	2, III A	652.59	$a^4F_{2½}$—$x^2F^0_{2½}$		
57.85	25	60, III	659.03	$a^4F_{2½}$—$y^4P^0_{2½}$	(0.00) 1.53	(0.00) 1.54
30.64	1		754.27			
23.56	3	3, III	779.22	$b^2D_{1½}$—$w^2P^0_{1½}$		
21.34	1		787.04	$a^2P_{1½}$—$w^2D^0_{2½}$		
20.14	3	3, III	791.28	$a^4F_{3½}$—$z^2G^0_{3½}$		
07.52	3	3, III	835.96			
5,304.01	20	30, III	848.43	$a^4P_{1½}$—$y^4P^0_{2½}$		
5,287.45	1	1, V	907.46			
76.40	5	10, III	947.06	$b^2D_{1½}$—$w^2F^0_{2½}$	(0.00) 0.90	(0.00) 0.90.
71.18	100	150, I	18,965.82	$a^2D_{2½}$—$y^2P^0_{1½}$	(0.00) 1.39 A[2]	(0.00) 1.44 A[2]
57.83	4	3, III	19,013.98		(0.00) 1.07	
53.45	100	100, I	029.83	$a^2D_{2½}$—$y^4F^0_{1½}$	(0.23, 0.69) 0.57, 1.03, 1.49, 1.95	(0.21, 0.63) 0.57, 0.99 1.41, 1.83.
40.81	4	2, III	075.72			
39.54	4	4, III	080.35	$a^2F_{3½}$—$y^2G^0_{3½}$		
34.27	150	300, II	099.56	$a^4F_{4½}$—$1^0_{4½}$	(0.00 W) 2.10 A[2]	(0.00) 2.10 A[2].
5,211.85	150	300, II	187.72	$a^4F_{4½}$—$y^4D^0_{3½}$	(0.00 W) 1.73 A[2]	(0.00) 1.71 A[2].
5,190.34	8		261.21			
83.91	10	20, II	285.10	$a^2D_{2½}$—$y^4F^0_{2½}$		
79.11	2	2, III	302.98	$b^2D_{1½}$—$5^0_{1½}$		
77.30	150	300, II	309.72	$a^4F_{3½}$—$y^4D^0_{2½}$	(0.00) 1.07	(0.00) 1.06.
68.95	2		340.92	$a^2F_{3½}$—$w^2F^0_{3½}$		
67.79	20	20, III	345.26	$a^4F_{4½}$—$2^0_{4½}$		
64.03		1, V?	359.34	$b^2D_{2½}$—$t^2F^0_{3½}$		
61.54	2		368.68			
58.68	40	80, I	379.42	$a^2D_{1½}$—$y^2D^0_{1½}$	(0.19, 0.57) 1.05, 1.45, 1.85	(0.20, 0.60) —, 0.98, 1.38, 1.78
52.31	1		403.38	$a^2F_{3½}$—$y^4G^0_{3½}$		
45.42	100	200, II	429.36	$a^4F_{2½}$—$y^4D^0_{1½}$	(0.00) 0.89	(0.00) 0.90)
39.16	3		453.03			
35.42	3	2, V	467.20			
34.37	2		471.18			
29.81	3		488.48			
20.87	10	10, III	522.51	$b^2D_{1½}$—$w^2D^0_{1½}$	(0.00) 0.92	(0.03) 0.90
09.12	3	2, III A	567.40	$a^2F_{3½}$—$y^2G^0_{4½}$		
06.23	100	150, II	578.48	$a^4F_{1½}$—$y^4D^0_{0½}$	(0.19) 0.62 A[2]?	(0.19) 0.22, 0.60
5,103.11	3	2, III	590.45			
5,096.59	2	1, IV?	615.51			
86.22	2		655.50	$z^4F^0_{2½}$—35		
79.37	4	5, IV	682.01			
78.92	3	2, V?	683.76			
72.10	3	1, III A	710.22	$a^2D_{2½}$—$y^4F^0_{3½}$		
67.90	15	15, III	726.56	$a^4F_{3½}$—$1^0_{3½}$		
56.46	60	80, II	771.18	$a^4F_{1½}$—$y^4D^0_{1½}$	(1.20) 0.00, 0.79, 1.57	(0.39, 1.19) 0.02, 0.81, 1.60
52.10	1		788.25	$b^2D_{2½}$—$z^2D^0_{1½}$		
50.57	60	80, II	794.24	$a^4F_{3½}$—$y^4D^0_{2½}$	(0.80) 1.18 B	(–, –, 0.79) —, 0.88, 1.19, 1.51, —
46.87	30	60, III	808.75	$a^4F_{3½}$—$y^4D^0_{3½}$	(0.00 w) 1.24	(0.00) 1.22
37.60	2		845.20	$a^2P_{1½}$—$6^0_{0½}$		
33.24	2		862.40			
19.50	10	8, III	916.76			
5,001.78	20	10, III A	19,987.32	$a^2F_{3½}$—$w^2F^0_{3½}$		
4,995.95	1		20,010.64	$a^2F_{2½}$—$y^4G^0_{3½}$		
94.64	2	1, III A	015.90	$b^2D_{2½}$—$w^4D^0_{1½}$		
93.87	15	20, II	018.98	$a^2D_{1½}$—$y^2P^0_{1½}$		
84.92	3	2, IV?	054.92	$a^4F_{3½}$—$3^0_{3½}$		
84.63	1		056.09	$a^2P_{1½}$—$e^2D^0_{2½}$		
83.56	2		060.40	$b^2D_{1½}$—$w^2D^0_{2½}$		
77.95	8	8, II A	083.01	$a^2D_{1½}$—$y^4F^0_{1½}$		
68.59	4 d	2{III A, V}	120.84	$a^2F_{3½}$—$y^2G^0_{4½}$		

TABLE 6.—*The arc spectrum of lanthanum (La I)*—Continued

λ_{air} I. A.	Intensities, temperature class		ν_{vac} cm^{-1}	Term combination	Zeeman effects	
	B. S.	K. & C.			Observed	Computed
64.84	3	4, III A	136.03	$a^4F_{1½}-y^4D^0_{½}$		
57.77	4		164.75			
49.76	50	200, I	197.38	$a^2D_{1½}-y^2P^0_{½}$	(0.00) 0.84	(0.00) 0.84
45.84	3	5, III A	213.39	$a^2F_{2½}-w^2P^0_{1½}$		
25.40	3	2, IV	297.27			
16.62	3	1, III? A	333.52			
05.13	4	4, III A	381.15	$a^2F_{2½}-u^2F^0_{½}$		
4,901.87	15	25, I	394.70	$a^2D_{2½}-z^2G^0_{4½}$	(0.00) 0.94	(0.00) 0.92
4,894.24	2	1, III	426.49			
87.60	4	5, III	454.24	$a^2F_{2½}-w^2D^0_{2½}$		
86.82	3	2, IV	457.51			
81.94	1		477.96	$a^4P_{1½}-w^2D^0_{1½}$		
78.86	10	15, III	490.89	$a^2F_{2½}-f^2F^0_{3½}$	(0.00) 1.10 R	(0.18) 1.10
70.56	5	5, III	525.81	$b^2D_{1½}-p^2D^0_{1½}$		
68.90	3	2, IV?	532.80			
67.37	3		539.26	$a^4F_{2½}-3^0_{3½}$		
54.95	8	8, III	591.80	$b^2D_{2½}-p^2D^0_{2½}$	(0.00) 1.21 R	(0.35) 1.21
50.81	20	20, I	609.37	$a^2D_{2½}-x^2F^0_{3½}$		
39.51	20	25, II	657.49	$a^2F_{2½}-f^2F^0_{2½}$	(0.00) 0.89	(0.04) 0.89
17.55	3		751.66			
17.17	10	4, IV?	753.29	$b^2D_{2½}-7^0_{1½}$		
4,800.24	9	8, III	826.49	$a^4P_{2½}-w^2D^0_{2½}$		
4,799.99	8	8, III	827.57	$a^2G_{3½}-s^2F^0_{3½}$		
92.46	1	tr, III A	860.30	$a^4F_{1½}-x^4D^0_{½}$		
91.77	1		863.30	$a^4P_{2½}-f^2F^0_{3½}$		
91.39	5	5, II	864.96	$a^4F_{2½}-w^2F^0_{3½}$		
79.89	4	4, II	915.16	$a^4F_{3½}-w^2F^0_{3½}$		
75.14	3	2, V	935.96	$a^2G_{3½}-9^0_{3½}$		
70.43	10	15, II	956.63	$a^2F_{2½}-w^2D^0_{1½}$	(0.00) 0.93 R	(0.00) 0.89
67.80	1 h		968.19	$a^4F_{4½}-z^2H^0_{4½}$		
66.89	60	100, I	20,972.19	$a^2D_{1½}-x^2F^0_{2½}$	(0.00) 0.99	(0.00) 0.98
59.71	2	2, IV?	21,003.83	$a^2G_{3½}-s^2F^0_{3½}$		
57.14	3	2, IV	015.18			
56.97		1, V	015.93	$a^4P_{1½}-w^2D^0_{2½}$		
53.11	2	1, IV	032.99			
52.41	3	3, III	036.09	$a^4F_{1½}-x^4D^0_{2½}$		
50.41	10	15, III	044.95	$a^2G_{4½}-s^2F^0_{3½}$	(0.00) 1.04 R	(0.00) 1.02
33.82	8	4, V?	118.70	$b^2D_{2½}-6^0_{3½}$		
29.09	1	1, V	139.82			
23.72	2	3, II	163.86	$a^4F_{2½}-4^0_{1½}$		
14.14	4	5, I	206.86	$a^4F_{1½}-w^2F^0_{2½}$		
08.18	8	8, III?	233.71	$b^2D_{2½}-8^0_{1½}$	(0.00) 0.97 R	(0.00) 1.15
02.64	8	10, I	258.72	$a^4F_{4½}-x^4F^0_{4½}$		
4,700.26	8	8, III?	269.48			
4,695.30	3		291.95	$a^4P_{2½}-p^2D^0_{1½}$		
60.70	8	8, III	450.02	$a^2F_{2½}-w^4D^0_{3½}$	(0.00) 0.92 R	(0.00) 0.92
53.90	4		481.36	$a^4P_{1½}-p^2D^0_{1½}$		
52.07	15	20, I	489.81	$a^4F_{3½}-x^4F^0_{3½}$		
50.32	12	15, I	497.90	$a^4F_{2½}-p^2F^0_{3½}$	(0.30) 1.13	(0.37) 1.12
48.64	30	40, I	505.67	$a^4F_{1½}-4^0_{1½}$	(0.48)	(0.15, 0.46) 0.26, 0.57, 0.87
46.33	10	12, III	516.36	$a^2G_{3½}-r^2F^0_{3½}$	(0.00) 0.89 R	(0.00) 0.95
43.11	5	5, III	531.28	$a^2F_{2½}-f^2F^0_{3½}$		
27.35	2		604.61	$b^2D_{2½}-s^2F^0_{3½}$		
15.06	8	15, III	662.14	$a^4P_{½}-w^4D^0_{½}$	(1.31) 1.37 R	(1.35) 1.35
05.08	6	10, III	709.09	$a^4P_{1½}-w^4D^0_{1½}$		
04.24	6	10, III	713.05	$b^2D_{2½}-9^0_{3½}$		
4,602.04	10	20, III	723.43	$a^2F_{2½}-e^2D^0_{2½}$		
4,596.19	6	10, I	751.08	$a^2D_{2½}-y^4D^0_{2½}$		
89.89	5		780.93	$b^2D_{2½}-s^2F^0_{2½}$		
81.20	10	12, III	822.25	$a^4P_{2½}-w^4D^0_{2½}$		
70.02	60	250, I	875.63	$a^4F_{4½}-x^4F^0_{4½}$	(0.00) 1.34	(0.11) 1.34
67.90	50	200, I	885.78	$a^4F_{3½}-x^4F^0_{3½}$	(0.00) 1.24	(0.02) 1.23
64.85	6	12, III	900.41	$a^4F_{3½}-x^4F^0_{2½}$	(0.00) 1.42 R	(0.15, 0.45) 1.18, 1.48
52.47	8	8, II A	959.96	$a^2F_{2½}-p^2D^0_{1½}$	(0.00) 0.87	(0.00) 0.87
50.76	8	10, III A	968.21	$a^4P_{½}-w^4D^0_{1½}$	(0.78) 0.38 R	(0.77) 0.38, 1.93

TABLE 6.—*The arc spectrum of lanthanum (La I)*—Continued

λ_{air} I. A.	Intensities, temperature class		ν_{vac} cm^{-1}	Term combination	Zeeman effects	
	B. S.	K. & C.			Observed	Computed
50.16	4	5, III A	971.11	$a^4F_{1½}-z^4S_{1½}$		
49.50	40	50, I	21, 974.30	$a^4F_{2½}-x^4F^0_{1½}$	(0.00) 1.08	(0.17) 1.07
41.78	10	15, III	22, 011.65	$a^4P_{1½}-w^4D^0_{2½}$		
37.57	2		032.07	$a^2P_{1½}-u^2D^0_{1½}$		
28.88	3		074.34	$a^4P_{1½}-6^0_{½}$		
07.4	2		179.5	$a^2G_{3½}-r^2F^0_{3½}$		
01.57	6	10, II A	208.26	$a^4F_{2½}-x^2D^0_{2½}$		
4,500.21	30	40, II	214.97	$a^4P_{2½}-w^4D^0_{3½}$	(0.00 w) 1.10 A[1]	(0.12, 0.37–) 0.67, 0.92, 1.17–, –, –
4,499.04	10	10, III	220.75	$a^2G_{4½}-r^2F^0_{3½}$	(0.00) 1.02	(0.00) 1.02
94.71	20	30, I	242.16	$a^4F_{1½}-x^4F^0_{½}$	(0.51) 0.27, 0.58, 0.91 us	(0.16, 0.47) 0.26, 0.57, 0.88
93.81	5	10, I A	246.61	$a^2D_{1½}-y^4D^0_{½}$	(0.00) 0.72 R	(0.38) 0.42, 1.17
93.11	15	25, I	250.08	$a^2D_{2½}-y^4D^0_{1½}$	(0.00) 1.16	(0.04) 1.21
91.76	10	15, III	256.76	$a^4F_{2½}-7^0_{1½}$	(0.00) 1.52	(0.00) 1.54
86.06	10	20, III	285.04	$a^4P_{1½}-v^2D^0_{2½}$		
79.82	6	15, II A	316.08	$a^4F_{1½}-x^4F^0_{2½}$		
74.54	4	5, III A	342.42	$b^2D_{1½}-s^2F^0_{2½}$		
68.97	10	25, II	370.26	$a^4F_{2½}-z^4F^0_{2½}$		
55.21	3	10, II A	439.35	$a^2D_{1½}-y^4D^0_{1½}$		
53.85		2, IV A	446.20	$a^4P_{1½}-7^0_{1½}$		
52.15	15	30, II	449.78	$a^2G_{3½}-y^2H^0_{2½}$	(0.00) 0.98	(0.00) 0.97
45.12	2	2, III A	490.29	$a^2F_{2½}-w^4D^0_{3½}$		
43.94	5	10, I	496.26	$a^2D_{2½}-3^0_{2½}$		
42.68	6	12, II	502.64	$a^4F_{2½}-z^4F^0_{3½}$		
23.90	20	30, II	598.16	$a^2G_{4½}-y^2H^0_{3½}$	(0.00) 1.09	(0.00) 1.09
17.14	2	6n, III	632.75	$a^4F_{2½}-y^4P^0_{1½}$		
13.45		2, III A	651.67	$a^2D_{2½}-x^4D^0_{1½}$		
03.02	2	8, III A	705.33	$a^4P_{½}-7^0_{1½}$		
4,402.64	5	15, III	707.29	$a^2P_{½}-u^2D^0_{1½}$	(0.00) 0.86	(0.00) 0.86
4,397.04		2, IV A	736.21	$a^2F_{2½}-s^2F^0_{2½}$		
96.79		4, IV A	737.50	$a^4P_{2½}-8^0_{1½}$		
96.31		2, IV	739.98			
93.52	2	4, III	754.42			
89.87	6	15, III	773.34	$a^2P_{1½}-u^2D^0_{2½}$	(0.00) 1.07	(0.00) 1.06
80.55	4	12, II A	821.79	$a^2D_{2½}-w^2F^0_{2½}$		
60.86	2	2, III A	924.84	$a^2F_{2½}-7^0_{1½}$		
60.49	2	2, III A	926.78	$a^4P_{1½}-8^0_{½}$		
57.88	2	2, III A	940.51	$a^4F_{2½}-x^2F^0_{1½}$		
54.79	20	25, III	22, 956.79	$b^2D_{1½}-r^2F^0_{2½}$		
40.72	10	15, III	23, 031.20	$b^2D_{1½}-r^2F^0_{3½}$	(0.00) 0.90	(0.00) 0.87
39.93	5	6, III A	035.39			
26.19	2		108.55	$a^4P_{2½}-s^2F^0_{2½}$		
11.73	5	4, III A	186.05	$a^4P_{½}-8^0_{½}$	(0.59) 0.96 R	(0.58) 0.96, 2.12
06.00	6	6, II A	216.90	$a^4P_{2½}-9^0_{2½}$	(0.14) 1.49	(0.20) 1.50
4,300.62	HNR	3	245.94	$a^2P_{½}-v^2P^0_{½}$		
4,291.00	2		298.06	$a^4P_{1½}-s^2F^0_{2½}$		
89.65	HNR	1	305.39	$b^2D_{1½}-u^2D^0_{1½}$		
89.01	HNR	2	308.87	$b^2D_{2½}-u^2D^0_{2½}$		
80.27	60	100, I	356.46	$a^2D_{2½}-w^2F^0_{3½}$	(0.00) 1.14	(0.00) 1.13
71.14	4		406.39	$a^4P_{1½}-9^0_{2½}$		
67.74	2		425.04	$a^2F_{3½}-r^2F^0_{3½}$		
62.35	10	15, II A	454.66	$a^2D_{2½}-v^2F^0_{2½}$	(0.00 w) 1.19	(0.00) 1.20
56.92	6	6, III A	484.58	$a^2P_{1½}-v^2P^0_{1½}$	(0.00) 1.29 R	(0.08) 1.29
38.59	4	10, III A	586.13	$a^2D_{2½}-z^4S^0_{1½}$		
4,216.54	4		709.47	$a^2D_{2½}-x^2D^0_{1½}$		
4,192.72	HNR	2	844.17	$b^2D_{1½}-v^2P^0_{½}$		
87.31	50	125, I	874.98	$a^2D_{1½}-w^2F^0_{2½}$	(0.00 w) 1.16 A[2]	(0.00) 1.16 A[2]
77.48	15	30, I	931.15	$a^2_1D_{2½}-x^4F^0_{1½}$	(0.00) 1.50 (?)	(0.20) 1.16
72.32	6	10, III A	960.75	$a^4F_{3½}-y^4G^0_{3½}$		
71.13	5	8, III A	23, 967.58	$a^4F_{4½}-y^4G^0_{4½}$		
63.31	5	8, III A	24, 012.60	$a^4F_{3½}-y^4G^0_{2½}$		
60.26	20	30, I	030.21	$a^2D_{2½}-x^4D^0_{3½}$	(0.00 w) 1.65 w	(0.00) 1.67
57.52	6	10, II A	046.04	$a^2D_{1½}-x^4D^0_{1½}$		

TABLE 6.—*The arc spectrum of lanthanum (La I)*—Continued

λ air I. A.	Intensities, temperature class		ν vac cm^{-1}	Term combination	Zeeman effects	
	B. S.	K. & C.			Observed	Computed
50.24	2		088.22	$a^3F_{3\frac{1}{2}}-r^3F^0_{1\frac{1}{2}}$		
44.36	4		122.40	$a^4F_{3\frac{1}{2}}-y^3G^0_{3\frac{1}{2}}$		
43.92	5	12, III A	124.96	$a^4F_{3\frac{1}{2}}-y^3G^0_{4\frac{1}{2}}$		
37.05	20	40, I	165.02	$a^3D_{2\frac{1}{2}}-x^4D^0_{3\frac{1}{2}}$	(0.00) 1.22	(0.09) 1.23
17.67	8	20, III	278.75		(0.00) 0.93	
09.80	10	20, I A	325.24	$a^3D_{2\frac{1}{2}}-v^3F^0_{1\frac{1}{2}}$	(0.00) 1.04	(0.00) 1.04
09.48	6	15, II A	327.14	$a^3D_{2\frac{1}{2}}-x^4F^0_{1\frac{1}{2}}$	(0.00) 1.26	(0.00) 1.22
4,104.87	30	60, I	354.46	$a^4F_{1\frac{1}{2}}-y^4G^0_{2\frac{1}{2}}$	(0.08, 0.25) 0.53, 0.69, 0.85 ur	(0.07, 0.23) 0.34, 0.49, 0.64, 0.80
4,090.40	2		440.61	$a^3F_{3\frac{1}{2}}-u^3D^0_{2\frac{1}{2}}$		
89.61	25	50, I	445.33	$a^4F_{2\frac{1}{2}}-y^4G^0_{3\frac{1}{2}}$	(0.00) 0.93	(0.00) 0.94
79.17	20	40, I	507.90	$a^3D_{1\frac{1}{2}}-v^3F^0_{2\frac{1}{2}}$		
65.58	15	30, II	589.82	$a^3D_{2\frac{1}{2}}-y^4P^0_{1\frac{1}{2}}$		
64.79	25	50, II	594.60	$a^4F_{3\frac{1}{2}}-y^4G^0_{3\frac{1}{2}}$	(0.00 w) 1.03 A[1]	(0.00) 0.94 A[1]
60.33	30	60, II	621.61	$a^4F_{4\frac{1}{2}}-y^4G^0_{3\frac{1}{2}}$	(0.00 w) 1.10 A[1]	(0.00) 1.12 A[1]
40.97	2		739.57	$a^3F_{3\frac{1}{2}}-u^3D^0_{1\frac{1}{2}}$		
37.21	25	50, I	762.61	$a^3D_{1\frac{1}{2}}-x^3D^0_{2\frac{1}{2}}$	(0.00) 0.86	(0.13) 0.84
15.39	25	50, I	897.17	$a^3D_{2\frac{1}{2}}-x^3P^0_{2\frac{1}{2}}$	(0.10, 0.31) 0.90, 1.10, 1.30, 1.48 ur	(0.10, 0.30) 0.90, 1.10, 1.30, 1.51
4,001.38	2		24,984.34	$a^3D_{1\frac{1}{2}}-x^4F^0_{1\frac{1}{2}}$		
3,953.67	10	40, II	25,285.83	$a^3D_{2\frac{1}{2}}-y^4F^0_{2\frac{1}{2}}$		
27.56	30	80, I	453.92	$a^3D_{1\frac{1}{2}}-x^3P^0_{0\frac{1}{2}}$	(0.00) 0.76	(0.00) 0.76
3,902.57	5	20, II	616.91	$a^3D_{1\frac{1}{2}}-y^4P^0_{0\frac{1}{2}}$		
3,898.60	8	40, II	25,642.99	$a^3D_{1\frac{1}{2}}-y^4P^0_{1\frac{1}{2}}$		
3,895.65		8?, IV	25,662.42			
3,714.30	2		26,915.34	$a^3D_{2\frac{1}{2}}-w^3D^0_{1\frac{1}{2}}$		
3,704.54	10	40, II	26,986.25	$a^3D_{2\frac{1}{2}}-u^3F^0_{3\frac{1}{2}}$	(0.00) 1.08	(0.00), 1.04
3,699.57	4	12, II A	27,022.51	$a^3D_{1\frac{1}{2}}-y^4G^0_{2\frac{1}{2}}$		
72.02	8	30, II	225.24	$a^3D_{1\frac{1}{2}}-w^3P^0_{1\frac{1}{2}}$		
49.55	10	40, II	392.86	$a^3D_{1\frac{1}{2}}-u^3F^0_{2\frac{1}{2}}$	(0.00) 1.00	(0.00) 0.98
41.53	20?	100, II	453.19	$a^3D_{2\frac{1}{2}}-w^3D^0_{2\frac{1}{2}}$		
36.67	6	40, III	489.88	$a^3D_{2\frac{1}{2}}-t^3F^0_{3\frac{1}{2}}$		
3,613.08	10	30, II	669.36	$a^3D_{1\frac{1}{2}}-t^3F^0_{2\frac{1}{2}}$	(0.00) 0.97	(0.00) 0.90
3,574.43	20	50, II	27,968.53	$a^3D_{1\frac{1}{2}}-w^3D^0_{1\frac{1}{2}}$	(0.00) 0.83	(0.17) 0.85
3,514.07	6	20, II A	28,448.92	$a^3D_{2\frac{1}{2}}-w^4D^0_{3\frac{1}{2}}$		
3,480.61	3	8, III A	722.40	$a^3D_{2\frac{1}{2}}-v^3D^0_{3\frac{1}{2}}$		
61.18	10	25, III A	883.64	$a^3D_{2\frac{1}{2}}-7^0_{1\frac{1}{2}}$		
50.65	5	12, III A	28,971.78	$a^3D_{1\frac{1}{2}}-v^3D^0_{1\frac{1}{2}}$		
3,404.53	10	15, III A	29,364.24	$a^3D_{2\frac{1}{2}}-8^0_{1\frac{1}{2}}$		
3,388.61	6	12, II A	502.18	$a^3D_{1\frac{1}{2}}-w^4D^0_{2\frac{1}{2}}$		
81.42		15, II A	564.92	$a^3D_{1\frac{1}{2}}-6^0_{1\frac{1}{2}}$		
68.36	3		679.54	$a^3F_{3\frac{1}{2}}-11^0$		
64.88	2		710.24	$a^3F_{3\frac{1}{2}}-10^0$		
62.04	7	12, III A	735.33	$a^3D_{2\frac{1}{2}}-s^3F^0_{3\frac{1}{2}}$		
57.50	5	7, III A	775.54	$a^3D_{1\frac{1}{2}}-v^3D^0_{2\frac{1}{2}}$		
49.82	2	3, III A	843.80	$a^3D_{2\frac{1}{2}}-0^0_{2\frac{1}{2}}$		
3,342.23	10	20, II A	29,911.57	$a^3D_{2\frac{1}{2}}-s^3F^0_{2\frac{1}{2}}$	(0.00) 1.08	(0.00) 1.14
3,256.60	2		30,698.05			
47.06	5	8, II A	788.24	$a^3D_{1\frac{1}{2}}-s^3F^0_{2\frac{1}{2}}$		
35.66	3	5, III A	30,896.71	$a^3D_{1\frac{1}{2}}-9^0_{2\frac{1}{2}}$		
3,215.81	10	15, II A	31,087.42	$a^3D_{2\frac{1}{2}}-r^3F^0_{2\frac{1}{2}}$	(0.00) 1.13	(0.00) 1.14
3,179.78	4	8, III A	439.65	$a^3D_{2\frac{1}{2}}-u^3D^0_{3\frac{1}{2}}$		
75.99	8	15, II A	477.17	$a^3D_{1\frac{1}{2}}-r^3F^0_{2\frac{1}{2}}$		
48.51	4	4, III A	31,751.89	$a^3D_{1\frac{1}{2}}-u^3D^0_{1\frac{1}{2}}$		
3,109.42	8	12, II A	32,151.04	$a^3D_{2\frac{1}{2}}-v^3P^0_{1\frac{1}{2}}$		
3,096.02	8	10, II A	32,290.19	$a^3D_{1\frac{1}{2}}-v^3P^0_{0\frac{1}{2}}$		
10.78	4	2, IV A	33,204.34	$a^3D_{1\frac{1}{2}}-v^3P^0_{1\frac{1}{2}}$		
3,001.41	2		307.99			
2,992.99	2		33,401.69			
09.65	2		34,358.36			
2,904.62	1		34,417.85			
2,817.46	2		35,482.54			
2,794.03	4		35,780.07			
66.46	4		36,136.62	$a^4F_{3\frac{1}{2}}-13^0$		
61.56	7		200.74	$a^4F_{4\frac{1}{2}}-14^0$		

TABLE 6.—*The arc spectrum of lanthanum (La I)*—Continued

λ air I. A.	Intensities, temperature class		ν vac cm^{-1}	Term combination	Zeeman effects	
	B. S.	K. & C.			Observed	Computed
59.54	4		227.24			
56.57	2		266.27			
49.52	2		359.25			
39.25	4		495.56			
37.49	3		519.03			
30.15	2		617.20			
29.85	5		621.22	$a^4F_{3½}$—13°		
25.57	15		678.73	$a^3D_{3½}$—11°		
22.31	6		722.65	$a^3D_{1½}$—10°		
17.33	2		789.90			
15.77	3		811.08			
14.52	8		828.03	$a^4F_{3½}$—14°		
10.69	4		880.06			
2,707.07	3		36,929.38	$a^4F_{1½}$—12°		
2,684.11	6		37,245.25			
77.77	2		333.43	$a^4F_{2½}$—15°		
71.91	2		415.30			
53.48	2		675.16	$a^4F_{1½}$—15°		
47.13	2		765.53			

V. IONIZATION POTENTIALS OF LANTHANUM ATOMS

The first two members of series have been identified in the spectra of lanthanum in all three degrees of ionization, and the ionization potentials for three different lanthanum atoms, La, La^+, La^{++}, may thus be deduced spectroscopically from extrapolation of the series to their limits.

To use the Rydberg formula is equivalent to assuming that the denominator n^* changes by exactly 1 from one term to the next in a series. In those spectra for which long series and accurate limits are available, the change Δn^* between the first and second members is usually somewhat greater and it appears to be preferable to assume that the value for lanthanum is comparable with that for similar spectra. For example, in the 1-electron spectra we find the following values of Δn^* for the s electron:

K I	Ca II	Rb I	Sr II	Cs I	Ba II
1.031	1.033	1.040	1.042	1.050	1.052

We may therefore assume $\Delta n^* = 1.050$ for La III. The terms 6^2S and 7^2S then give a limit at 154,630 (above the lowest level $^2D_{1½}$) with $n^* = 2.6462, 3.6962$. This corresponds to an ionization potential of 19.07 volts which is the lowest known value for a third ionization. Badami [26] from his analysis of this spectrum derived 20.4 volts for the ionization potential of La^{++}.

[26] J. S. Badami, Proc. Phys. Soc. London, vol. 43, p. 53, 1931.

For 2-electron spectra we find for the ^3S and ^3D terms due to "running" s and d electrons:

Term	^3S			^3D		
Spectrum	Ca I	Sr I	Ba I	Ca I	Sr I	Ba I
Δn^*	1.040	1.042	1.045	1.135	1.181	1.289

The ^1S and ^1D series in the alkaline earths are too much perturbed[27] to be of use. We therefore assume that in La II $\Delta n^* = 1.05$ for a running s electron; that is, for the terms a^3D, f^3D, and a^1D, f^1D, with limit 5^2D in La III, and 1.15 for a running d electron (a^3D, h^3D with limit 6^2S). The resulting values of n^* (referred to the proper limit for each component) and of the difference between the lowest level in La II (a^3F_2) and La III ($5^2D_{1½}$) are as follows:

Term	$^3D_1$	$^3D_2$	$^3D_3$	$^1D_1$	$^3D_1$	$^3D_2$	$^1D_3$
n^*	2, 2232	2, 2333	2, 2206	2, 1826	2, 0384	2, 0453	2, 0518
	3, 2732	3, 2833	3, 2706	3, 2326	3, 1884	3, 1953	3, 2018
Limit	90, 704	90, 600	90, 664	91, 924	93, 944	93, 924	93, 916

The mean of these seven values is 92,240, which corresponds to an ionization potential of 11.38 volts for La^+.

Finally, for La I, we have the terms a^4F, e^4F and a^2F, e^2F with a running s electron and limit a^3F of La II. With limit a^3D we have only a^2D and e^4D, but these terms, though of different multiplicity, may still be used.[28] The first comes from the configuration $5d\ 6s^2$, the second from $5d\ 6s\ 7s$. Dropping the $5d$ electron we obtain the lowest ^1S and ^3S terms in Ba I. For these and the corresponding terms in Ca I and Sr I we have the values of n^*.

Spectrum	Ca I	Sr I	Ba I
$n^*(^1S)$	1.442	1.545	1.616
$n^*(^3S)$	2.484	2.548	2.629
Δn^*	1.042	1.003	1.013

We may, therefore, adopt $\Delta n^* = 1.010$ in this case while in the others we use 1.060. We then find

Term	$a^2D_{3½}$ $e^4D_{3½}$	$a^4F_{1½}$ $d^4F_{1½}$	$a^4F_{2½}$ $e^4F_{2½}$	$a^4F_{3½}$ $e^4F_{3½}$	$a^4F_{4½}$ $e^4F_{4½}$	$a^2F_{3½}$ $e^2F_{2½}$	$a^2F_{1½}$ $e^2F_{1½}$
n^*	1.5221	1.6033	1.6000	1.5948	1.5892	1.6829	1.6855
	2.5321	2.6633	2.6600	2.6548	2.6492	2.7429	2.7455
Limit	45, 145	45, 337	45, 856	45, 606	45, 583	44, 721	44, 687

The mean is 45,293 for the interval from $a^2D_{1½}$ (La I) to a^3F_2 (La II). This corresponds to an ionization potential of 5.59 volts.

A change of +0.01 in Δn^* alters the computed limits on the average by −152 or −0.019 volts. The average discordance of the seven

[27] A. G. Shenstone and H. N. Russell, Phys. Rev., vol. 39, p. 415, 1932.
[28] We owe this suggestion to Prof. A. G. Shenstone.

determinations from the mean is ± 334 or ± 0.041 volts. We, therefore, adopt 5.59 ± 0.03 volts as the first ionization potential of lanthanum. This is in excellent agreement with the value 5.49 volts derived by Rolla and Piccardi [29] from observations of the ionization current and rate of dissociation of La_2O_3 in flames.

For La II a change in Δn^* by ± 0.01 affects the ionization potential by ± 0.044 volts, while the average discordance of one determination is ± 0.13 volts.

We may finally adopt for lanthanum atoms:

First ionization potential $= 5.59 \pm 0.03$ volts.
Second ionization potential $= 11.38 \pm 0.07$ volts.
Third ionization potential $= 19.1 \pm 0.1$ volts.

VI. DISCUSSION OF ZEEMAN EFFECTS

The observed Zeeman effects for lanthanum lines in all three spectra positively identify most of the spectral terms although a comparison of the observed and theoretical g values discloses many discrepancies which greatly exceed the experimental errors. Similar deviations have been observed in other spectra, and have been assigned either to departures from strict SL coupling, or to the sharing of g values by mutually perturbing terms. If the coupling between spin moment and orbital moment of each electron is weak individually as compared with the coupling of the spins and those of the orbital moments of the electrons mutually we have the so-called SL coupling:

$$\{(s_1\ s_{2\text{----}})\ (l_1\ l_{2\text{----}})\} = (SL) = J$$

An atom for which this is true will emit a spectrum in which interval rules, and Zeeman effects are in accord with the values predicted by the theory of Landé and others. But if the quantum vectors s and l are actually compounded to produce a resultant vector J in some other manner the spectrum will show violations of the interval rules and deviations from Landé's g values. Such deviations are evident in the La spectra. For example, the metastable quartet-F term in the La I spectrum shows only a slight departure from the interval rule:

	Separations	Ratios
Theoretical	$^4F_{4½}-{}^4F_{3½}:{}^4F_{3½}-{}^4F_{2½}:{}^4F_{2½}-{}^4F_{1½}=$	9.00:7.00:5.00
La I	627.0 : 484.6 : 341.8 =	9.00:6.95:4.90

and the observed g values are almost exactly those of Landé

Level	Observed g	Landé g
$^4F_{1½}$	0.411	0.400
$^4F_{2½}$	1.032	1.029
$^4F_{3½}$	1.222	1.238
$^4F_{4½}$	1.337	1.333

The low terms in the La II spectrum do greater violence to the interval rule, and also somewhat larger divergences of observed and theoretical

[29] L. Rolla and G. Piccardi, Phil. Mag., vol. 7, p. 286, 1929.

g values occur. Thus, for the normal state represented by a^3F we have the following interval ratios:

	Separations	Ratios
Theoretical	$^3F_4-^3F_3:^3F_3-^3F_2$	4.00:3.00
La II	954.6 : 1016.1	4.00:4.26

and the following g values:

Level	Observed g	Landé g
$^3F_2$	0.730	0.667
$^3F_3$	1.092	1.083
$^3F_4$	1.258	1.250

Similarly for the term a^3D, the interval ratios are:

	Separations	Ratios
Theoretical	$^3D_3-^3D_2:^3D_2-^3D_1$	3.00:2.00
La II	658.8:696.4	3.00:3.17

and the splitting factors are:

Level	Observed g	Landé
$^3D_1$	0.520	0.500
$^3D_2$	1.140	1.167
$^3D_3$	1.337	1.333

These, and many other departures from theoretical values indicate a considerable deviation from (SL) coupling, probably in the direction of (jj) coupling defined, in the case of two electrons, by

$$\{(s_1l_1)\ (s_2l_2)\} = (j_1j_2) = J$$

in which the interactions between spin and orbital moment of each electron predominate.

No matter what the nature of the coupling may be the so-called g-sum rule of Pauli[30] is expected to be valid. This rule can be stated as follows: If, among all the terms arising through the coupling of one electron, those terms with the same inner quantum number J be grouped, the sum of the g values of the terms in each group must have a value independent of the nature of the coupling, and consequently is, among others, equal to the sum of the Landé g values for a similar group. This rule is tested in Table 7 where the observed and Landé g sums are displayed for all the groups in La II for which the data are complete and for the low terms in La I, although one term has not been found. The sums of observed g values are slightly larger than the theoretical sums, but the differences can perhaps be ascribed to the accumulation of a small systematic error of observation. If the observered g's are diminished by 0.78 per cent, to allow for this, the agreement becomes almost perfect, with an average discordance of only 0.5 per cent.

[30] W. Pauli, Zeits. f. Phys., vol. 16, p. 155, 1923.

TABLE 7.—*Zeeman effect: Sums of adopted and Landé g values*

La II

Electrons	Terms	J = 6 Adopted	6 Landé	5 Adopted	5 Landé	4 Adopted	4 Landé	3 Adopted	3 Landé	2 Adopted	2 Landé	1 Adopted	1 Landé	Sum Adopted	Sum Landé
ds	a^3D							1.337	1.333	1.140	1.167	0.520	0.500	2.997	3.000
	a^1D									.987	1.000			.987	1.000
d^2	a^3F					1.258	1.250	1.092	1.083	.730	.667			3.080	3.000
	a^1P									1.488	1.500	1.506	1.500	2.994	3.000
	a^1G					1.003	1.000							1.003	1.000
	b^1D									1.015	1.000			1.015	1.000
Sum low terms						2.261	2.250	2.429	2.416	5.360	5.334	2.026	2.000	12.076	12.000
pf	e^3G			1.203	1.200	1.146	1.050	.873	.750					3.222	3.000
	e^3F					1.141	1.250	1.061	1.083	.732	.667			2.934	3.000
	e^3D							1.306	1.333	1.100	1.167	.495	.500	2.901	3.000
	e^1G					1.060	1.000							1.060	1.000
	e^1F							.953	1.000					.953	1.000
	e^1D									1.046	1.000			1.046	1.000
ds	f^3D							1.331	1.333	1.141	1.167	.520	.500	2.992	3.000
	f^1D									1.020	1.000			1.020	1.000
Sum all even terms				1.203	1.200	5.608	5.550	7.953	7.916	10.399	10.335	3.041	3.000	28.204	28.000
sf	z^3F					1.26	1.25	1.09	1.08	.67	.67			3.02	3.00
	z^1F							1.05	1.00					1.05	1.00
df	z^3H	1.17	1.17	1.08	1.03	.86	.80							3.11	3.00
	z^3G			1.20	1.20	1.06	1.05	.77	.75					3.03	3.00
	y^3F					1.24	1.25	1.09	1.08	.76	.67			3.09	3.00
	z^3D							1.32	1.33	1.19	1.17	.55	.50	3.06	3.00
	z^3P									1.46	1.50	1.46	1.50	2.92	3.00
	z^1H			1.00	1.00									1.00	1.00
	z^1G					1.00	1.00							1.00	1.00
	y^1F							1.03	1.00					1.03	1.00
	z^1D									.93	1.00			.93	1.00
	z^1P											.88	1.00	.88	1.00
dp	x^3F					1.25	1.25	1.08	1.08	.84	.67			3.17	3.00
	y^3D							1.31	1.33	1.19	1.17	.80	.50	3.30	3.00
	y^3P									1.49	1.50	1.26	1.50	2.75	3.00
	x^1F							1.06	1.00					1.06	1.00
	y^1D									.90	1.00			.90	1.00
	y^1P											1.07	1.00	1.07	1.00
ds	x^3P									1.48	1.50	1.52	1.50	3.00	3.00
	x^1P											.97	1.00	.97	1.00
Sum all odd terms		1.17	1.17	3.28	3.23	6.67	6.60	9.80	9.66	10.91	10.84	8.51	8.50	40.34	40.00

TABLE 7.—*Zeeman effect: Sums of adopted and Landé g values*—Continued

La I

Electrons	Terms \ J	4½		3½		2½		1½		½		Sum	
		Adopted	Landé	Adopted	Landé	Adopted	Landé	Adopted	Landé	Adopted	Landé	Adopted	Landé
ds^2	a^2D					1.20	1.20	0.79	0.80			1.99	2.00
d^2s	a^4F	1.33	1.33	1.22	1.24	1.03	1.03	.41	.40			3.99	4.00
	a^4P					1.54	1.60	1.69	1.73	2.71	2.67	5.94	6.00
	a^2G	1.12	1.11	.91	.89							2.03	2.00
	a^2F			1.13	1.14	.90	.86					2.03	2.00
	b^2D					1.29	1.20	.89	.80			2.18	2.00
	a^2P							1.32	1.33	.67	.67	1.99	2.00
	^2S									(2.00)	2.00	(2.00)	2.00
Sum low terms		2.45	2.44	3.26	3.27	5.96	5.89	4.31	4.26	3.38	3.34	20.15	20.00

WASHINGTON, August 6, 1932.

RP498

ANALYSIS OF WEIGHTED SILK

By Ralph T. Mease

A generally applicable, rapid, and convenient method for the determination of the amount of pure silk fiber in silk textiles is described. Weighting and finishing materials are removed by repeated extractions with hot water, 2 per cent sodium carbonate solution and a solution containing 2 per cent of hydrochloric and 2 per cent of hydrofluoric acids. Results of analyses of samples of known composition are presented which indicate that the results are correct to within 1 per cent of the weight of the dried finished material. Results obtained by inexperienced analysts working in different laboratories have been in good agreement when samples of the same silk were analyzed. Qualitative methods for the identification of the following weighting materials are given: Aluminum, lead, phosphate, silica, tin, zinc.

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I. INTRODUCTION

Raw silk, as it comes to the manufacturer, contains about 75 per cent fiber (fibroin) and about 25 per cent gum (sericin) exclusive of moisture. At some stage of the processing the gum is removed by "boiling off" in a soap solution. The silk may then be "weighted" by the addition of various metallic salts or other substances, the amount of the weighting being determined by the purposes for which the silk is intended, the selling price, and similar considerations. The amount of weighting added seldom is less than the amount of the gum removed and it may exceed the amount of the silk fibroin. The claim is made that weighted silk has a better "hand" or "feel" than unweighted silk, that it drapes better, and that its lower cost makes possible the use of silk by persons who otherwise could not afford it.

After weighting, the silk may be dyed, or printed. It is finally "finished" by the addition of gums, soaps, waxes, hygroscopic substances, or other "finishing" materials which contribute to the desired properties.

The need for a standard method of analysis for weighted silk arose several years ago when special attention was being given to the problem of overweighting. There was an insistent demand from numerous manufacturers, distributors, and consumers for definite limits on the amount of weighting to be allowed on different types of silk fabrics. This led to the tentative designation of limits by the Silk Association of America in January, 1929.[1] In order to insure satisfactory analyses of weighted silks for conformance with these standards or other standards that might be agreed upon, attention

[1] Fifty-seventh Annual Report, Silk Association of America, New York, p. 27, 1929.

was given by a Technical Committee on Weighted Silk [2] to methods of analysis. A proposed standard method was published.[3]

The proposed standard method was the one in common use calling for extraction with hydrofluoric acid, amplified to make possible the successful analysis of silks weighted with materials other than tin-phosphate-silicate. When samples of silk of known weighting content were submitted to cooperating laboratories for analysis by this method, the results were in error in one instance by no less than 32 per cent of the amount actually present and in two other instances by 17 and 20 per cent.[4]

In anticipation of the need for analyses of weighted silks in several projects in the textile section of the Bureau of Standards, and with the expectation that the Federal Trade Commission would require analyses of weighted silks, some attention was given to the development of a generally applicable and satisfactory method. This work resulted in a method which is reasonably rapid, convenient, and reliable. The work is described and the resulting method is given in this paper. Qualitative tests that have been found useful in identifying inorganic weighting materials on silk are also given.

II. EXPERIMENTAL STUDIES

The important determination in the analysis of weighted silk is that of fibroin content. Several methods have been proposed for obtaining this value. In one method [5] the fibroin is evaluated by determining nitrogen, which is a constituent of silk fibroin. This value is in error if dyestuffs containing nitrogen are present in the silk. In another method [6] the fibroin content is indirectly evaluated by making a determination of the ash content of the weighted silk. This is done by igniting a sample in air. The weighting materials are changed during the ignition and the weight of the ash is not a true measure of the weighting materials contained in the material. A third method, which is also indirect, consists in the extraction of inorganic materials with hydrofluoric acid.[7] When lead, zinc, or aluminum salts are present, however, the material is alternately treated with hydrofluoric and hydrochloric acids. Neither of these last two treatments entirely removes the inorganic materials.

It was found in this laboratory that a solution containing 2 per cent of hydrofluoric and 2 per cent of hydrochloric acids was more effective in removing inorganic weighting materials than either acid alone, or the alternate treatments with these two acids. Furthermore, the combination of hydrofluoric and hydrochloric acids was found to be less destructive to silk fibroin than hydrochloric acid alone.

Unweighted silk cloth was purified by boiling it in several changes of neutral soap solution, then extracting with alcohol to remove soap,

[2] The Joint Committee of the Textile Industry on Weighted Silk, composed of representatives from national associations representing manufacturers, distributors, and users, established this smaller technical committee to consider technical problems.

[3] Anon, To find silk weighting content, Textile World, vol. 76, p. 1454, Sept. 14, 1929.

[4] Unpublished data of the Technical Committee on Weighted Silk.

[5] Gnehm, R., and Blummer, E., Méthode pour le dosage de la charges des soies noires, Rev. gén. mat. color., vol. 2, pp. 133–134, April, 1898.

[6] Branegan, James A., Practical analysis of methods for determination of artificial weighting of tin weighted silk, Melliand, vol. 1, pp. 735–739, August, 1929. Compares results obtained with several methods of analysis.

[7] Gnehm, R., Eine neue Methode zur quantitativen Bestimmung der Zinn-Phosphat-Silicat-Charge auf Seide, Z. Farben-Textil-Chem., vol. 2, pp. 209–210, June 1, 1903.

and finally with ether. It was then immersed in boiling water and finally dried in air at room temperature. This silk is referred to as "silk fibroin" in the experiments to be described.

The first step in the analysis of weighted silk by extraction with hydrofluoric acid is the removal of soluble finishing materials; that is, materials soluble in water or organic solvents that might be expected to be removed by either wet washing or dry cleaning. The purpose is not only to obtain a value for the amount of such materials, but to expose the insoluble weighting to more ready attack in subsequent treatments. Rinsing of the specimen with alcohol and ether to complete the removal of soluble finishing materials and to expedite the drying was found to be unsatisfactory because silk fibroin may hold these solvents even when dried above their boiling points. This was demonstrated in the following experiments.

Samples of silk fibroin weighing about 2.5 g each were dried to constant weight (±0.1 per cent) in an air oven at 105° to 110° C. The time required was 1 to 1½ hours. Weighings were made at one-half hour intervals up to five hours. These samples were then soaked in 100 times their weight of distilled water at 65° C. for 20 minutes, rinsed in a fresh portion of distilled water, then in alcohol and finally in ether, a procedure typical of those used for soluble finishing materials. They were then dried to constant weight as before. The dry weight of the samples thus treated was approximately 1.5 per cent more than the weight of the original dry material. The samples were then immersed in boiling water and again dried. After this treatment the samples were found to have returned to their original weight. This procedure was repeated and it was clearly evident that when the silk was rinsed in alcohol and then in ether before drying, the weight of the dry material was considerably higher than when the silk was rinsed finally in boiling water. It was also found by other experiments that the alcohol and ether could be removed by water at temperatures below boiling. On this evidence, the final rinse in alcohol and ether must be followed by immersion of the specimens in water before drying.

After removal of soluble finishing materials, weighting is removed in the hydrofluoric acid method by alternate treatments of the silk with dilute hydrofluoric acid and dilute sodium carbonate solutions. Various concentrations, temperatures, and times of treatment are used in different laboratories. According to the method recommended by the Technical Committee on Weighted Silk, silk weighted with tin phosphate without silicate requires a treatment with dilute hydrochloric acid solution as well as with hydrofluoric acid.

Preliminary experiments indicated that both the concentration and temperature of the reagents are extremely important, too drastic treatment materially affecting the silk fibroin and too mild treatment not removing the weighting completely. Further, a mixture of hydrofluoric and hydrochloric acids [8] was found to be more efficient and less harmful than the separate treatments with hydrochloric and hydrofluoric acids called for in the method of the technical committee.

The treatments which were finally adopted are described in Section III. The effects of these treatments on silk weighted in several differ-

[8] Suggested informally several years ago by Dr. Victor Froelicher, chief chemist, Textile Dyeing Co. of America.

ent ways likely to be encountered in practice [9] are shown in Table 1. The amount of silk fibroin found by analysis of silk of known weighting content agreed with the amount present within 1 per cent of the weight of the dry finished silk for tin phosphate, logwood black, and other types of weighting as well as for the usual tin-phosphate-silicate weighted silk. The average loss in weight of eight samples of silk fibroin, when given the treatment for removing weighting, was 0.49 per cent and the maximum loss was less than 1 per cent.

Analyses of over 75 samples of commercial weighted silks have been made according to the method by several analysts, with excellent results. The amount of dry silk fibroin obtained in duplicate determinations agrees well within 1 per cent of the weight of the dried sample. The ash obtained by igniting the sample after treatment for removal of weighting seldom exceeds 0.1 per cent and is usually very much less than this when the silk is weighted with tin-phosphate-silicate.

Results of a few analyses of commercial samples made independently by analysts of two laboratories using different kind of equipment are given in Table 2.[10] Evidently good results may be obtained without the use of special equipment.

TABLE 1.—*Results of analyses of weighted silks*

[Values are in percentages of the weight of the ovendried specimen. Results of duplicate analyses given]

Sample No.	Type of weighting	Extraction with apparatus of Figure 1				Extraction with apparatus of Figure 3		
		Silk content	Soluble finishing materials	Residual ash	Silk fibroin	Soluble finishing materials	Residual ash	Silk fibroin
0	Tin phosphate	60.4	4.3 4.5	1.2	61.0 60.8			
1	Tin phosphate silicate	48.3	4.5 3.7	.0	48.6 49.1	3.4 4.2	0.5	50.2 49.2
2	Tin phosphate, lead, silicate	50.8	4.5 5.1	.8	50.9 50.8	4.7 4.6	.1	52.8 52.6
3	Tin phosphate logwood black	52.1	4.9 5.2	.1	53.0 53.0	2.7 3.4	.1	53.0 54.3
4	Tin phosphate silicate	50.1	4.7 4.7	.1	50.5 49.9			
5	Tin phosphate zinc	60.9	5.2 5.3	.0	60.6 60.8			
10	Commercial silk, tin phosphate silicate	Unknown.	4.8 4.9	.0	48.4 48.0	4.2 3.9	.0	48.1 48.4
11	do	Unknown.	6.3 6.0	.0	50.2 51.0	5.8 5.7	.0	50.9 51.1
12	do	Unknown.	5.2 6.6	.0	60.0 59.2	4.6 5.2	.0	59.0 59.0
13	do	Unknown.	6.8 6.5	.0	92.5 92.3	3.4 4.9	.0	93.5 93.1
14	do	Unknown.	5.5 5.4	.1	49.1 49.4	4.7 5.2	.1	48.3 48.6
15	do	Unknown.	5.5 5.2	.0	42.2 42.3	5.3 4.6	.0	41.6 41.2
16	do	Unknown.	5.4 5.2	.0	50.5 50.0	4.8 5.9	.1	49.6 49.3
17	do	Unknown.	6.8 6.4	.0	55.2 55.2	5.0 5.6	.1	54.9 55.2

[9] The author is indebted to Dr. Victor Froelicher for the samples of known weighting content representative of the different types of weighting.

[10] These results were obtained under the supervision of Prof. Pauline Beery Mack, of the department of home economics, Pennsylvania State College.

TABLE 2.—*Results of analyses by two independent laboratories on commercial silks*

[Values are for silk fibroin expressed as percentages of the weight of the ovendried specimen]

Sample No.	By Bureau of Standards extraction with apparatus of Figure 3	By Pennsylvania State College laboratory inexperienced analyst with no special equipment	Sample No.	By Bureau of Standards extraction with apparatus of Figure 3	By Pennsylvania State College laboratory inexperienced analyst with no special equipment
41	98.8	99.3	51	97.2	98.3
42	91.5	91.8	52	91.8	92.0
43	62.0	61.6	53	65.4	67.2
44	57.7	58.3	54	58.2	58.9
45	49.4	48.7	55	54.8	55.6
46	49.3	48.3	56	49.4	50.8
47	47.5	46.8	57	48.5	50.0
48	43.8	43.3	58	41.4	42.9

III. A METHOD FOR THE ANALYSIS OF WEIGHTED SILK

The specimen for analysis should be representative of the cloth. A strip the full width of the cloth is suggested and should weigh from 3 to 5 g.

The specimen is dried at 105° to 110° C. to constant weight (±0.1 per cent). If the specimen is loosely spread on a watch glass and placed in the usual laboratory electric oven at 105° to 110° C., it should dry within one and one-half hours. It is then placed in a tared weighing bottle, allowed to cool in a desiccator, and weighed. The weight of the dry specimen is called weight A.

Soluble finishing materials are removed by the following treatments. The specimen is immersed for about two minutes each in two 30 ml portions of diethyl ether at room temperature, squeezing by hand after each immersion. Then it is treated similarly with two 30 ml portions of ethyl alcohol at 50° to 60° C. Finally it is immersed in 90 to 100 times its weight of distilled water at 65° to 70° C. for 20 minutes, squeezed by hand, and rinsed by immersion for about one-half minute each in three fresh portions of distilled water at the same temperature, squeezing by hand after each immersion. It is then dried at 105° to 110° C. as before. The weight of the dry specimen at this stage is called weight B.

Weight A − weight B × 100/weight A = soluble finishing materials in per cent (based on the weight of the dried specimen).

The more firmly held weighting and finishing materials are now removed by the following series of treatments: (*a*) The specimen is immersed in 90 to 100 times its weight of a solution [11] containing 2 per cent of hydrofluoric acid and 2 per cent of hydrochloric acid maintained at a temperature of 55° C. ± 1° C. The acid liquid is decanted and the specimen is rinsed with two portions of distilled water at 55° to 60° C. squeezing by hand after each rinse. (*b*) The

[11] This reagent may conveniently be prepared by mixing equal volumes of 4 per cent (±0.1 per cent) hydrofluoric and 4 per cent (±0.1 per cent) hydrochloric acids. High concentrations of mineral acids disintegrate silk. Too low a concentration may not remove inorganic materials sufficiently well from all types of weighted silk fabrics. For this work the concentration of each of the acids was determined by titration with a standard base. The concentrations given mean per cent by weight of actual HF and HCl (not of the ordinary concentrated acids). The reagent is approximately *N* with respect to HF and *N*/2 with respect to HCl.

treatment with acid solution (fresh solution) followed by rinsing is repeated. (*c*) This treatment is again repeated using a 2 per cent solution of sodium carbonate in place of the acid solution. (*d* and *e*) The treatment with acid solution is then applied two times more. (*f*) The specimen is then rinsed several times with distilled water and is dried as previously described. The dry weight is called weight C. Provided all materials other than silk fibroin have been removed

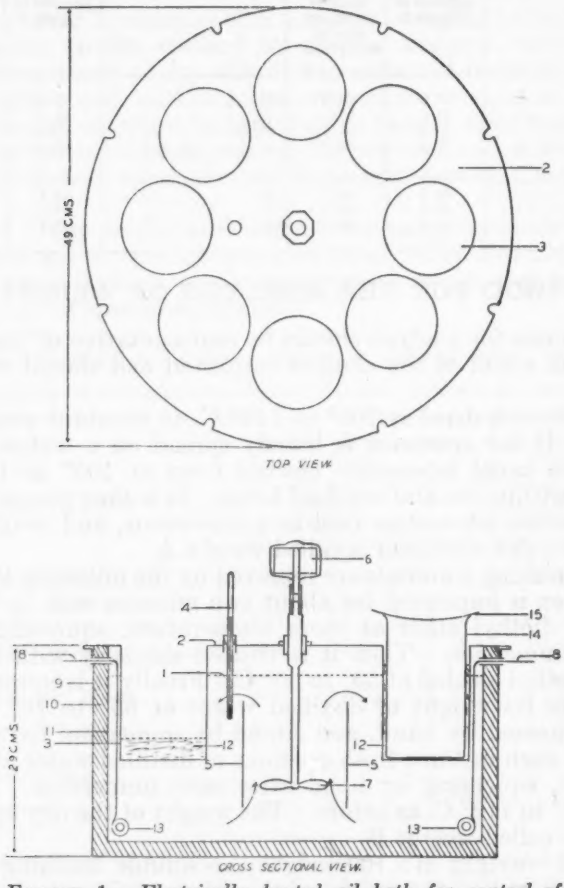

FIGURE 1.—*Electrically heated oil bath for control of the temperature of the solutions during the extraction process*

1, level of oil in the bath; 2, metal cover; 3, body of water bath container; 4, thermometer; 5, wall of cylinder to guide the circulating oil; 6, electric motor; 7, propeller blade for agitating the oil bath; 8, glass insulated electric leads to heater coil; 9, outer wall of metal container; 10, mineral wool for heat insulation; 11, inner wall of double-jacketed metal container; 12, water bath; 13, nichrome wire heating coil—1 unit of a 3 and 1 of a 4 amp current consumption at 110 v; 14, 800 ml Pyrex beaker, tall form; and 15, watch glass cover.

(see suggestions for ashing the specimen below), then: Weight C×100/weight A=silk fibroin in per cent (based on the weight of the dried specimen).

Weight A−weight C×100/weight A=total weighting in per cent (based on the weight of the dried specimen).

The total weighting thus obtained includes all substances other than silk fibroin.

Weighting is adequately removed from some silks when steps (*b*) and (*e*) are omitted, but these steps are necessary for the complete removal of weighting from others. It is advisable to determine the ash as a check on the effectiveness of the extraction. Ashing is done preferably by heating the specimen in a well ventilated muffle furnace. If the weight of the ash is more than 0.2 per cent it should be subtracted from the value obtained for weight C in the formulas.

The simple oil bath shown in Figure 1 is a convenience if a number of analyses are to be made. With it the temperature of the solutions can readily be controlled to within 1° C. and eight specimens can be handled simultaneously.

When many samples are to be analyzed time may be saved by using a battery of semiautomatic extraction units. One of these units, constructed of thick walled Pyrex glass, is shown in Figure 2. The specimens to be extracted are placed loosely in the tube, *F*.

Apparatus of the dimensions indicated will hold five specimens. The liquid is placed in the 1-liter flask, heated to the proper temperature, and the flask is inverted in the position shown at *A*. The orifice, *D*, is of such size that 15 to 20 minutes are required for the flask to empty. The extraction is not always quite so thorough with this apparatus as when the specimens are treated individually in beakers in the constant temperature bath.

Concentrated hydrofluoric acid may be measured with a pipette like that shown in Figure 3. Such a pipette may be made of Pyrex glass and coated on the inside by drawing melted ozokerite into the

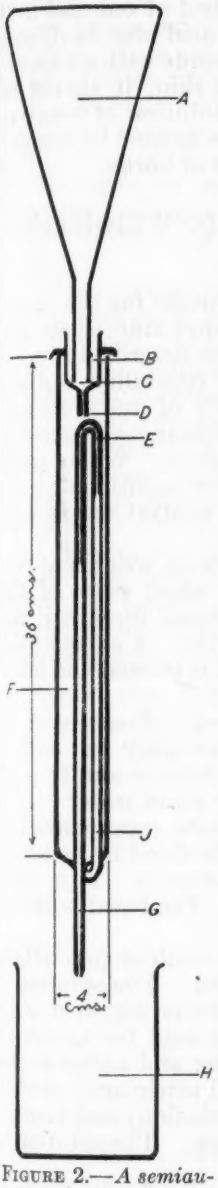

FIGURE 2.—*A semiautomatic extraction apparatus for analysis of weighted silk*

A, 1,000 ml Erlenmeyer flask; *B*, trap; *C*, outlet for liquid and inlet for air to flask *A*; *D*, capillary tube controlling flow of liquid; *JEG*, siphon tube; *F*, chamber for samples; and *H*, reservoir for spent liquor.

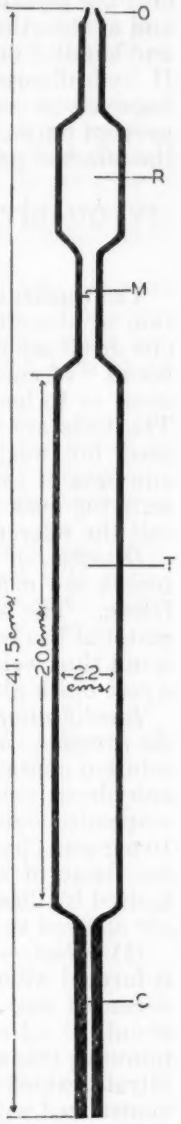

FIGURE 3.—*A pipette for transferring and measuring concentrated hydrofluoric acid*

T, main reservoir; *R*, auxiliary reservoir; *M*, calibration mark; *O*, suction orifice; and C, capillary discharge tube.

cold pipette and allowing the excess to drain. The acid is drawn into the pipette by means of a rubber tube attached at one end to 0 and at the other to the laboratory vacuum. The acid may be diluted and handled in a Pyrex beaker also coated on the inside with ozokerite. If hydrofluoric acid comes in contact with the skin, it should be removed as soon as possible by washing with a solution of borax to prevent burns. Hydrofluoric acid burns should be treated by keeping the affected parts moist with a saturated solution of borax.

IV. QUALITATIVE TESTS FOR INORGANIC WEIGHTING MATERIALS

The qualitative tests briefly described below provide for the detection of aluminum, lead, phosphate, silicate, tin and zinc when any one or all are present. They are based upon those described in textbooks [12] of chemical analysis and were chosen for reliability, convenience as to length of time required, and simplicity of manipulation. The tests are useful only for the detection of substances commonly used for weighting according to present practices. When small amounts of these substances are to be detected or additional or interfering ones are suspected of being present, the analyst should consult the references given in footnote 12.

Detection of inorganic materials in silk.—Inorganic weighting materials are conveniently detected by burning a small piece of the fabric. The ash will retain the form of the original threads if the material has been weighted with inorganic materials. A sample that is not thus weighted will curl back upon itself as it is burned and leave a soft black globular ash.

Identification of inorganic weighting materials—(*a*) *Preparation of the sample.*—A piece about 4 by 10 inches is thoroughly wet with a solution containing 90 g of anhydrous sodium carbonate and 90 g of anhydrous potassium carbonate, dissolved in 400 ml of water. It is suspended over a beaker containing 30 ml of dilute (approximately 10 per cent) hydrochloric acid solution and partially dried by brushing the flame of a hand torch or Bunsen burner across it. It is then ignited by directing the flame on the lower edge. The fused portions are allowed to drop into the acid in the beaker.

(*b*) *Silica.*—If silicates are present, a white flocculent precipitate is formed when the acid solution from (*a*) is boiled. The solution is decanted and filtered and the residue in the beaker digested with about 10 ml of warm concentrated hydrochloric acid for about 15 minutes; this acid is poured through the filter paper and added to the filtrate, which is boiled with 5 ml of concentrated nitric acid, cooled neutralized with sodium hydroxide (25 per cent solution) and enough hydrochloric acid added to produce a clear solution. The solution is used for tests (*c*) to (*g*) described below.

(*c*) *Lead.*—About 3 ml of the solution is neutralized with sodium hydroxide using phenolphthalein as an indicator. The solution is then made just acid with hydrochloric acid and about 1 ml of water saturated with hydrogen sulphide is added. If lead is present, a gray

[12] Prescott, Albert B., and Johnson, Otis C., Qualitative Chemical Analysis, 7th ed., thoroughly revised, 436 pp., 1916. D. Van Nostrand Co., New York. Scott, Wilfred W., Standard Methods of Chemical Analysis, 4th ed., vol. 1, 745 pp., 1925. D. Van Nostrand Co., New York. Hillebrand, W. F., and Lundell, G. E. F., Applied Inorganic Analysis, 929 pp., 1929. John Wiley & Sons (Inc.), New York

to black coloration is produced. (A yellow precipitate indicates the presence of tin.) If the sample of silk to be tested is light in color, it may be tested directly for lead by moistening it with water and exposing it to a jet of hydrogen sulphide gas. A change to gray or black indicates the presence of lead.

(*d*) *Aluminum.*—To about 3 ml of the solution, ½ ml of a saturated solution of ammonium chloride, ½ ml of alizarin (prepared by dissolving 0.1 g of the dye, Colour Index No. 1034 in distilled water), and an excess of ammonium hydroxide are added. The mixture is heated to boiling, an excess of glacial acetic acid is added, and the mixture diluted. A red flocculent precipitate denotes the presence of aluminum.

(*e*) *Tin.*—About 2 ml of the solution is neutralized with 25 per cent sodium hydroxide and about five drops in excess added. The solution is filtered, the filtrate acidified with hydrochloric acid, and a few drops of a 1 per cent water solution of cupferron added. A white precipitate indicates the presence of tin.

(*f*) *Zinc.*—About 3 ml of the solution is neutralized with 25 per cent sodium hydroxide, enough hydrochloric acid and water are added to produce a clear solution, and about ½ ml of a 2 per cent solution of potassium ferrocyanide is then added. A white precipitate indicates the presence of zinc.

(*g*) *Phosphate.*—About 2 ml of the solution is neutralized with sodium hydroxide and the resulting solution is acidified with nitric acid. It is heated and then added to an equal volume of hot acid ammonium molybdate. A lemon yellow precipitate is formed on standing if phosphates are present.

WASHINGTON, July 25, 1932.

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THE HEAT OF FORMATION OF HYDROGEN CHLORIDE AND SOME RELATED THERMODYNAMIC DATA

By Frederick D. Rossini

ABSTRACT

The calorimetric experiments of the present investigation give for the change in heat content associated with the formation of gaseous hydrogen chloride from its elements, at a constant pressure of 1 atmosphere, $\Delta H^\circ_{298.1} = -92.30 \pm 0.05$ international kilojoules mole^{-1}, or $-22{,}063 \pm 12$ g-cal.$_{15}$ mole^{-1}.

The existing data on the free energy and entropy of formation of gaseous hydrogen chloride are shown to be in accord, within the limits of uncertainty, with the above result. This correlation consists in bringing together (1) data on the emf of certain cells, (2) data on the vapor pressure of hydrogen chloride over its aqueous solution and the activity of aqueous hydrogen chloride, and (3) values of entropy which have been calculated from the data of spectroscopy.

Values of the apparent and partial molal heat capacity, and heat content, for hydrogen chloride, and of the partial molal heat capacity, and heat content, for water, in aqueous solution of hydrogen chloride at 25° C., are given for the entire range of concentration.

The change in heat content associated with the solution of 1 mole of gaseous hydrogen chloride in an infinite amount of water is calculated to be $\Delta H^\circ_{298.1} = -17{,}880 \pm 40$ g-cal.$_{15}$ mole^{-1}.

The change in heat content for the formation of silver chloride from its elements is given by: $\Delta H^\circ_{298.1} = -30{,}304 \pm 40$ g-cal.$_{15}$ mole^{-1}. For mercurous chloride the corresponding value is $\Delta H^\circ_{298.1} = -31{,}580 \pm 45$ g-cal.$_{15}$ mole^{-1}.

The change in heat content for the formation, from its elements, of aqueous hydrogen chloride at infinite dilution is given by: $\Delta H^\circ_{298.1} = -39{,}943 \pm 40$ g-cal.$_{15}$ mole^{-1}.

The free energy of formation of gaseous hydrogen chloride is calculated to be $\Delta F^\circ_{298.1} = -22{,}775 \pm 12$ g-cal.$_{15}$ mole^{-1}.

The entropy of aqueous hydrogen chloride, in a hypothetical 1 molal solution, is calculated to be: $S^\circ_{298.1} = 13.40 \pm 0.15$ g-cal.$_{15}$ mole^{-1} °C.$^{-1}$.

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I. INTRODUCTION

It has seemed desirable for a number of years that a new measurement be made of the heat of formation of hydrogen chloride, a fundamentally important chemical substance because it is one of the components of a number of chemical reactions having industrial and scientific importance, and because the value of its heat of formation is used in computing the heats of formation of practically all the metallic chlorides and of numerous other compounds.

The usually accepted value for the heat of formation of gaseous hydrogen chloride is based upon the work of Thomsen [1] in 1873. The pioneer work of Abria,[2] and of Favre and Silbermann,[3] gave values that are now obviously too high. The work of Berthelot [4] is difficult to appraise because of the lack of information concerning his experiments.

In effect, then, there is only one calorimetric investigation of the heat of formation of hydrogen chloride whose detailed data are available for appraisal and recalculation, and that work was performed 60 years ago.

An accurate calorimetric value of the change in heat content, ΔH, for the reaction

$$\tfrac{1}{2}H_2\ (\text{gas}) + \tfrac{1}{2}Cl_2\ (\text{gas}) = HCl\ (\text{gas}) \qquad (1)$$

is unusually interesting because of the opportunity it affords for correlating the thermodynamic data on this reaction by means of the relation [5]

$$\Delta H^\circ = \Delta F^\circ + T\Delta S^\circ \qquad (2)$$

where ΔF° and ΔS° are, respectively, the free energy and entropy of formation. The value of ΔS° is accurately known from the data of spectroscopy; [6] and the value of ΔF° is obtained by combining data on the emf of cells and the vapor pressure of hydrogen chloride over its aqueous solution.[7] Thus there is the interesting situation where the values of ΔH°, ΔF°, and ΔS° for the same reaction are obtained from totally independent sources:

ΔH°, from calorimetric measurements;
ΔS°, from spectroscopic data; and
ΔF°, from emf and vapor-pressure data.

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[1] Thomsen, J., Pogg. Ann., vol. 148, p. 177, 1873.
[2] Abria, Compt. rend., vol. 22, p. 372, 1846.
[3] Favre, P. A., and Silbermann, J. T., Ann. chim. phys., vol. 34, p. 357, 1852.
[4] Berthelot, M., Thermochimie (Gauthier-Villars, Paris), 1897.
[5] The thermodynamic symbols used in this paper will follow the nomenclature of Lewis and Randall, Thermodynamics and the Free Energy of Chemical Substances (McGraw-Hill Book Co., New York), 1923.
[6] Giauque, W. F., and Overstreet, R., J. Am. Chem. Soc., vol. 54, p. 1741, 1932.
[7] Randall, M., and Young, L. E., J. Am. Chem. Soc., vol. 50, p. 989, 1928.

These data should all agree, according to equation (2), within the limits of uncertainty of the weakest link in the chain.

Another interesting correlation can be made on the change in heat content for reaction (1) and the following:

$$\tfrac{1}{2}H_2\ (\text{gas}) + \tfrac{1}{2}Cl_2\ (\text{gas}) = HCl\ (\text{aqueous}) \quad (3)$$

$$HCl\ (\text{gas}) = HCl\ (\text{aqueous}) \quad (4)$$

For reaction (3) ΔH° can be computed from data on the temperature coefficient of the emf of cells, and for reaction (4) it is known from direct calorimetric measurements. The sum of the changes in heat content for reactions (1) and (4) should agree, within the limits of uncertainty, with the value of ΔH° for reaction (3). For this correlation there are required values of the apparent and partial molal heat content of hydrogen chloride in aqueous solution to infinite dilution, and the heats of formation of silver chloride and mercurous chloride.

With accurate values available for ΔH° and ΔF° it becomes possible to compute ΔS° for reaction (3), and consequently to obtain an accurate value of the entropy of aqueous hydrogen chloride in its standard state of a hypothetical 1 molal solution. This quantity serves as a basis for the calculation of the entropies of aqueous ions according to the methods used by Latimer and his coworkers.[8]

II. UNITS, FACTORS, ATOMIC WEIGHTS, ETC.

The fundamental unit of energy employed in the present calorimetric experiments is the international joule based upon standards of emf and resistance maintained at this bureau.[9]

The conversion factors used throughout this paper are:

1 international joule	= 1.0004 absolute joules
1 g-cal.$_{15}$	= 4.185 absolute joules
R (gas constant)	= 1. 9869 g-cal.$_{15}$ $^\circ C^{-1}$
F (Faraday constant)	= 23,067 g-cal.$_{15}$ (international volt-equivalent)$^{-1}$

The atomic weights of hydrogen and chlorine are taken from the 1932 report of the International Committee on Atomic Weights:[10] H, 1.0078; Cl, 35.457.

III. CALORIMETRIC DETERMINATION OF THE HEAT OF FORMATION OF HYDROGEN CHLORIDE

1. METHOD AND APPARATUS

The same calorimetric method and apparatus as were employed in determining the heat of formation of water were used in the present investigation,[11] with the exception that an automatic photo-electric regulator was used to maintain the temperature of the jacket constant

[8] Latimer, W. M., and Ahlberg, J. A., J. Am. Chem. Soc., vol. 54, p. 1900, 1932. References to the earlier publications are given in this paper.

[9] For a report on the international comparison of electrical standards, see Vinal, G. W., B. S. Jour. Research, vol. 8, p. 448, 1932.

[10] J. Am. Chem. Soc., vol. 54, p. 1269, 1932.

[11] Rossini, F. D., B. S. Jour. Research, vol. 6, p. 1, 1931; vol. 7, p. 329, 1931. The flow meters were removed from their previous positions and placed in the waste lines.

to ±0.001° C.[12] A platinum resistance thermometer, placed under the stirrer and heater in the water of the calorimeter jacket, served as one arm of a Wheatstone bridge whose unbalancing caused a shifting of a beam of light (reflected from a galvanometer mirror) on or off the photo-electric cell, which resulted in actuation of the relay and consequent stopping or starting of the regulatory flow of electrical current through the heater of the calorimeter jacket.

The calorimetric method is substantially the same as that of Thomsen. Chlorine is burned in an atmosphere of hydrogen, and the amount of reaction is determined from the mass of hydrogen chloride formed.

2. CHEMICAL PROCEDURE

(a) CHLORINE

Pure chlorine was obtained by decomposing potassium chloroplatinate which was carefully prepared from pure platinum, potassium chloride, and hydrochloric acid according to the procedure recommended by Noyes and Weber [13] in their work on the atomic weight of chlorine. The following reactions indicate the nature of the process used in the present investigation:

$$Pt\ (solid) + 6\ HCl\ (aqueous) = H_2PtCl_6\ (aqueous) + 2\ H_2\ (gas) \quad (5)$$

$$H_2PtCl_6\ (aqueous) + KCl\ (aqueous) = K_2PtCl_6\ (solid) + 2\ HCl\ (aqueous) \quad (6)$$

$$K_2PtCl_6\ (solid) = 2\ KCl\ (solid) + Pt\ (solid) + 2\ Cl_2\ (gas) \quad (7)$$

Each of the above reactions is practically complete and not complicated by any side reaction. The required reagents, platinum, potassium chloride, and hydrochloric acid, are obtainable in a very pure state.

Pure platinum was obtained from the platinum metals section of this bureau. It had been prepared according to the methods described by Wichers, Gilchrist, and Swanger.[14]

The potassium chloride was made by recrystallizing twice the best "reagent quality" potassium chloride. The most probable impurity in this material would be bromine, and tests indicated that this was present to the extent of 1 mole in 50,000 moles of potassium chloride.[15]

Aqueous hydrogen chloride was obtained by treating the best "reagent quality" hydrochloric acid with chlorine (made by the action of hydrogen chloride upon potassium permanganate) and then boiling off the dissolved chlorine. Tests of this aqueous hydrogen chloride indicated that the bromine present must have been less than 1 mole in 100,000 moles of hydrogen chloride.

The preparation of the chloroplatinic acid was carried out in the electrolytic cell of Weber, according to his directions, except that a current of 6 to 7 amperes instead of 10 was used.[16]

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[12] This regulator was of the type that has been described quite frequently in the past few years (see for example (*a*) Southard, J. C., and Andrews, D. H., J. Frank. Inst., vol. 207, p. 323, 1929; (*b*) Scott, R. B., and Brickwedde, F. G., B. S. Jour. Research, vol. 6, p. 401, 1931; (*c*) Beattie, J. A., Rev. Sci. Inst., vol. 2, p. 458, 1931). The author is indebted to E. N. Bunting for assembling the circuit of vacuum tubes, photo-electric cell, and relay.

[13] (*a*) Noyes, W. A., and Weber, H. C. P., J. Am. Chem. Soc., vol. 30, p. 13, 1908; B. S. Bull., vol. 4, p. 345, 1907–8. (*b*) Weber, H. C. P., J. Am. Chem. Soc., vol. 30, p. 29, 1908; B. S. Bull., vol. 4, p. 365, 1907–8.

[14] Wichers, E., Gilchrist, R., and Swanger, W. H., Trans. Am. Inst. Mining Met. Eng., vol. 76, p. 602, 1928.

[15] The tests for bromine were made according to Noyes, A. A., Qualitative Chemical Analysis (Macmillan Co., New York, N. Y.), 1925.

[16] The construction of the electrolytic cell had been improved by Edward Wichers, and the author is greatly indebted to him for his advice with regard to the preparation of the chlorine used in the present investigation.

The potassium chloroplatinate was made according to reaction (6), following the directions of Noyes and Weber except that the salt was washed with water only. The potassium chloroplatinate was then placed in an oven at 110° C. for several days to remove most of the moisture.

For carrying out reaction (7) the apparatus shown in Figure 1 was used. *A* is the furnace with electrical resistance heater; *B* is a silica flask containing the potassium chloroplatinate; *C* is a silica to Pyrex-glass seal; *D* is a trap for catching any potassium or platinum chlorides which might be volatilized; *E* is a condensing tube for collecting the chlorine; *G* is a connection to the vacuum system, which consists of a mercury vapor pump (properly trapped with liquid air) backed by an oil vacuum pump; *K* is a vacuum-tight Pyrex glass-to-copper

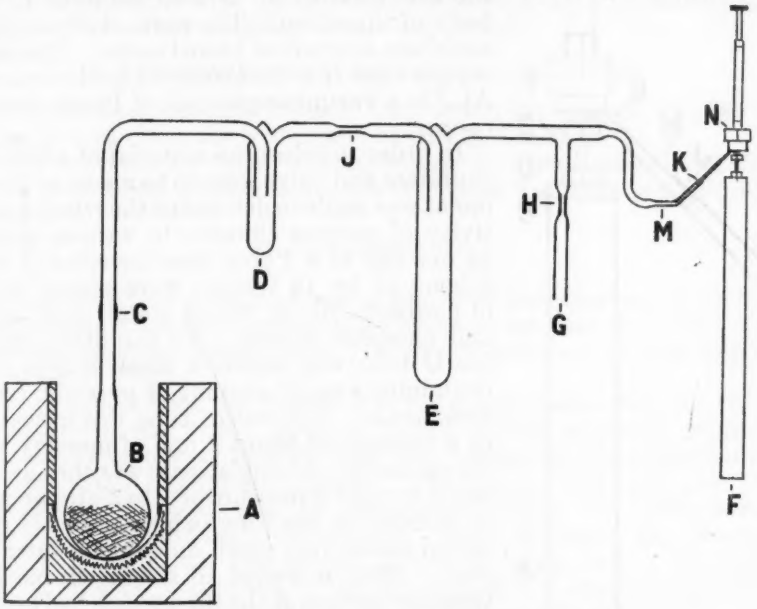

FIGURE 1.—*Apparatus for preparing pure chlorine*
The description is given in the text

seal; *F* is the Monel-metal container, having a Monel-metal diaphragm valve, in which the chlorine was finally stored.

The potassium chloroplatinate was heated to about 300° C. and the system kept evacuated to 0.0001 mm mercury for about three days. This was done to remove the last traces of water and hydrogen chloride from the solid. Then the constriction at *H* was sealed off. The flask *B* was heated to about 750° C. and liquid air placed around the condensing tube *E* where chlorine slowly began to collect as a solid. When chlorine no longer came over, the constriction at *J* was sealed off. The solid chlorine in *E* was liquefied and then distilled into the container *F*, the lower end of which was cooled with liquid air. When all but a small amount of the chlorine was collected in *F*, the valve *N* was closed and the glass system was broken at *M*. The chlorine container *F* was then sealed to the glass line leading to the calorimeter.

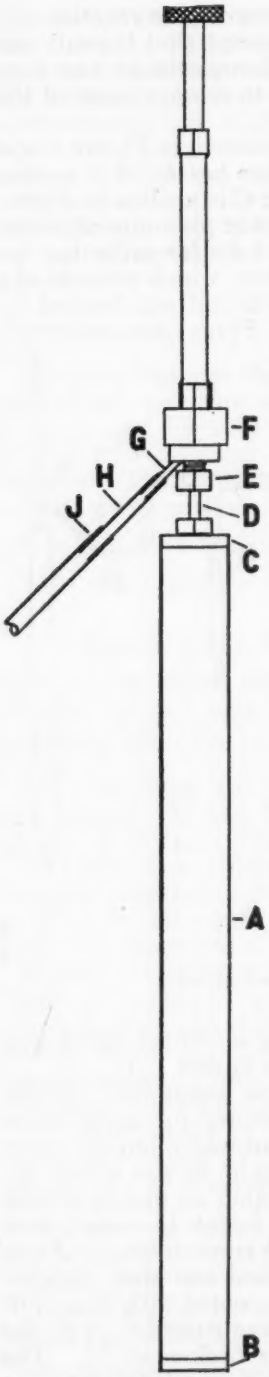

FIGURE 2.—*Chlorine container with diaphragm valve*

The description is given in the text.

A sketch of the chlorine container and valve is shown in Figure 2. *A* is the cylindrical body of the container. The end plugs *B* and *C* are screwed and silver soldered in place. The connecting tube *D* is screwed and silver soldered to the plug *C* and tightly connected to the valve *F* by means of the metal-to-metal connection at *E*. The valve *F*, which has a silver diaphragm and in which closures are made with Monel metal to silver seats, is one of the type used in the calorimetric researches on steam by Osborne, Stimson, and Fiock.[17] *G* is the exit tube which is lead soldered to the body of the valve. The parts *A*, *B*, *C*, *D*, *F*, and *G* are all made of Monel metal. The short copper tube *H* is lead soldered to the tube *G*.[18] At *J* is a vacuum-tight seal of Pyrex glass to copper.

In order to select the material of which the container and valve were to be made, an experiment was made to determine the relative reactivity of gaseous chlorine to various metals. In one end of a Pyrex glass inverted U tube (about 12 by 12 inches) were placed pieces of platinum, silver, Monel metal, steel, brass, and phosphor bronze. To the other end of the U tube was sealed a small quartz tube containing a small amount of potassium chloroplatinate. The entire tube was evacuated to a pressure of about 2 mm of mercury, and the potassium chloroplatinate was then decomposed to give a pressure of 1 to 2 atmospheres of chlorine in the tube (which probably contained also a very small amount of water vapor). After a period of about six months, visual inspection of the tube, which had been at room temperature, showed that the platinum and Monel metal were apparently unaffected by the chlorine, the silver and brass were very slightly coated with chloride, and the phosphor bronze and steel showed considerable evidence of reaction. When at the end of the first series of reaction experiments, which are to be described later, the Monel-metal valve was taken apart, the silver diaphragm and seat, as well as the Monel-metal surface of the interior of the valve, were found to have been unaffected by the chlorine.

[17] Osborne, N. S., Stimson, H. F., and Fiock, E. F., B. S. Jour. Research, vol. 5, p. 411, 1930. The success of the present experimental investigation was in large measure due to having a suitable container and valve for handling the chlorine, and the writer is greatly indebted to the heat measurements section for the loan of the Monel-metal diaphragm valve and the Monel-metal tube from which the container was made.

[18] The use of lead solder eliminates the possibility of forming the comparatively volatile stannic chloride.

(b) HYDROGEN

The hydrogen used in the present investigation was taken from a cylinder of commercial electrolytic hydrogen. Oxygen was removed from this gas by passage through a tube containing asbestos, impregnated with palladium, and quartz, impregnated with platinum, at about 500° C. Before entering the calorimeter, the gas then passed successively through "Ascarite" (a sodium-hydroxide asbestos mixture), "Dehydrite" ($Mg(ClO_4)_2 \cdot 3H_2O$), and phosphorus pentoxide.

Analyses of the hydrogen gas as it would enter the reaction chamber were made by the gas chemistry section. That part of the gas which was noncombustible with oxygen was found to be 0.0 ± 0.1 per cent. A test for the presence of carbon compounds in the hydrogen was made by burning it with a special sample of oxygen [19] and testing the exit gases for carbon dioxide. None was found.

(c) DETERMINATION OF THE AMOUNT OF REACTION

The amount of reaction in each combustion experiment was determined by absorbing the hydrogen chloride in "Ascarite."

With the absorber filled with hydrogen at 1 atmosphere and 25° C., and with brass weights in air, the true mass [20] of hydrogen chloride absorbed is

$$m_{(HCl)} = 0.99991 \Delta m \qquad (8)$$

where Δm is the observed increase in weight of the absorber, corrected for the small amount of unburned chlorine which was also absorbed. The determination of this latter quantity is described on page 686 of this paper.

In its passage from the container to the reaction chamber, the chlorine traversed one 2-way stopcock, which served to permit wasting immediately before the ignition and after the extinction of the flame, and two small ground-glass joints. Phosphoric acid was used to lubricate the stopcock and the two ground joints, the latter being lubricated anew for each experiment. With hydrogen gas flowing through the stopcock and ground joints so lubricated, a carefully weighed absorber connected to the exit end of the reaction chamber showed constancy of weight (± 0.1 mg per experiment, which is 1 part in 50,000).

The two ground joints on the exit side of the reaction chamber were lubricated with the same lubricant as previously used for nonreactive gases. In order to make sure that the lubricant on these two small ground joints would take up no appreciable amount of hydrogen chloride, the lubricant, spread over a large area, was exposed to hydrogen-chloride gas for the time of a calorimetric reaction experiment, and its change in weight determined. It was calculated that under the conditions of a calorimetric reaction experiment, the amount of hydrogen chloride taken up by the lubricant on the two ground joints was about 0.03 mg, or 1 part in 200,000.

Several experiments were made to determine the completeness of the removal, by the "Ascarite," of hydrogen chloride from the gas leaving the reaction vessel. In one experiment a concentrated aqueous solution of silver nitrate was placed beyond the absorber.

[19] See footnote 11, p. 681.
[20] See footnote 11, p. 681.

In another experiment a second absorber, carefully weighed, was placed in series with the first absorber. In both these experiments no hydrogen chloride passed the first absorber with the gas flowing at three or four times the rate actually used in the calorimetric experiments.

3. CALORIMETRIC PROCEDURE

(a) ELECTRICAL ENERGY EXPERIMENTS

These experiments were performed, as nearly as possible, over the same temperature range and with the same rate of temperature rise as the combustion experiments. The description of the procedure for the electrical energy experiments has already been given.[21]

The results of the electrical energy experiments are given in Table 1. The "error," computed [22] as

$$\pm 2\sqrt{\frac{(x-\bar{x})^2}{n(n-1)}}, \text{ is } \pm 0.014 \text{ per cent}$$

TABLE 1.—*Calorimetric results of the electrical energy experiments for hydrogen chloride*

Experiment No.	ΔR	k	u	K	U	Δt corr.	Average temperature	Electrical energy [1]	Mass of calorimeter water	Electrical equivalent of calorimeter system [2]	Deviation from mean
	ohm	*min.*$^{-1}$	*min.* $^{-1}$	*ohm*	*ohm*	° *C.*	° *C.*	*Int. joules*	*g*	*Int. joules* ° *C.*$^{-1}$	*joules* ° *C.*$^{-1}$
1	0.100338	0.001970	−0.0000084	0.002819	−0.000235	0.97044	30.00	14,988.3	3,620.53	15,359.1	2.7
2	.099976	.001945	−.0000035	.002810	−.000098	.96557	30.00	14,884.0	3,614.38	15,354.7	−1.7
3	.101019	.001934	.0000024	.002783	.000067	.97455	30.00	15,009.2	3,611.53	15,353.1	−3.3
4	.099545	.001947	.0000015	.002577	.000039	.96225	29.99	14,832.4	3,614.38	15,354.3	−1.9
5	.099308	.001966	−.0000032	.002617	−.000083	.96071	29.99	14,841.5	3,621.98	15,356.8	.6
6	.099320	.001968	.0000003	.002635	.000008	.95975	29.99	14,811.1	3,617.38	15,359.7	3.5
Mean										15,356.3	±2.3

[1] The time of electrical energy input was 1,320.00 seconds in experiments 1, 2, and 3, and 1,200.00 seconds in experiments 4, 5, and 6.
[2] Corrected to 3,600.00 g of water and an average temperature of 30.00° C.

(b) FIRST SERIES OF REACTION EXPERIMENTS

The amount of chlorine unburned during the time of ignition and extinction of the flame, was determined in "correction" experiments which consisted in ignition, burning for one or two seconds, and then extinction of the flame. The following data were required: (1) The increase in mass of the absorber, (2) the total energy imparted to the calorimeter by the reaction and the sparking operation (determined from the corrected temperature rise of the calorimeter and its electrical energy equivalent), and (3) the "spark" energy.

The "spark" energy was determined in two separate experiments to be 10.3 ± 0.1 joules for each sparking time of five seconds. From the energy imparted to the calorimeter by the reaction, which was the total energy less the "spark" energy and the "gas" energy,[23] the amount of hydrogen chloride formed was calculated. The differ-

[21] See footnote 11, p. 681. [22] See footnote 11, p. 681. [23] See footnote 11, p. 681.

ence between the mass actually taken up by the absorber and the mass of hydrogen chloride formed gave m_{Cl}, the mass of unburned chlorine.

In the first series of reaction experiments the chlorine which was in the burner tube at the time the flow of chlorine was cut off was not burned out, and consequently the value of m_{Cl} for these experiments is relatively large, being about one-half per cent of the total mass absorbed. The results of the "correction" experiments of the first series to determine the value of m_{Cl} are given in Table 2.

TABLE 2.—*Calorimetric results of the correction experiments for hydrogen chloride, first series*

Experiment No.	Number of ignitions and extinctions of flame	Total mass absorbed	Total energy	"Spark" energy	"Gas" energy	Mass of HCl	m_{Cl} per experiment
		g	*int. joules*	*joules*	*joules*	*g*	*g*
a	8	0.3749	473.1	82.4	−2.0	0.1551	0.0275
b	3	.1308	134.3	30.9	.3	.0411	.0299
c	3	.1408	156.5	30.9	.4	.0498	.0303
Mean							.0292

The calorimetric results of the first series of reaction experiments are given in Table 3. All the symbols are defined and explained in an earlier paper.[24] The only change from previous procedure was that the chlorine gas coming from the Monel metal container passed through a coil (about 9 feet long) of glass tubing immersed in a water bath maintained at the temperature of the room.

TABLE 3.—*Calorimetric results of the reaction experiments for hydrogen chloride, first series*

Experiment No.	ΔR	k	u	K	U	$\Delta t_{corr.}$	Average temperature
	ohm	min^{-1}	*ohm* min^{-1}	*ohm*	*ohm*	° *C.*	° *C.*
A	0.094404	0.001963	0.0000038	0.002473	0.000106	0.91157	30.00
B	.093969	.001923	−.0000040	.002461	−.000112	.90954	30.00
C	.095208	.001957	.0000001	.002422	.000003	.92109	30.00
Mean							

Experiment No.	Electrical equivalent of calorimeter system	Total energy	"Gas" energy	"Spark" energy	Mass of HCl formed	$Q_{300°C.}$, 1 atmosphere	Deviation from mean
	Int. joules ° $C.^{-1}$	*Int. joules*	*joules*	*joules*	*mole*	*Int. joules* $mole^{-1}$	*joules* $mole^{-1}$
A	15,418.2	14,054.8	39.2	10.3	0.152679	92,243	−143
B	15,494.4	14,092.8	40.4	10.3	.152770	92,445	59
C	15,432.0	14,214.3	43.8	10.3	.154078	92,471	85
Mean						92,386	±96

[24] See footnote 11, p. 681.

(c) SECOND SERIES OF REACTION EXPERIMENTS

In the second series of reaction experiments the chlorine remaining in the burner tube was all burned out by mixing hydrogen with the chlorine stream before the latter was cut off. This mixing was accomplished by opening the tube connecting the hydrogen and chlorine lines at their entrance into the calorimeter. Because of this improvement in the procedure, the value of m_{Cl} for the second series of reaction experiments was only about one-sixth of that for the first series, or about 0.08 per cent of the total mass absorbed; and a much greater precision was obtained in these experiments.

The results of the "correction" experiments of the second series are given in Table 4.

TABLE 4.—*Calorimetric results of the correction experiments for hydrogen chloride, second series*

Experiment No.	Number of ignitions and extinctions of flame	Total mass absorbed	Total energy	"Spark" energy	"Gas" energy	Mass of hydrogen chloride	m_{Cl} per experiment
		g	*Int. joules*	*joules*	*joules*	*g*	*g*
a	3	0.1652	412.1	30.9	−0.5	0.1508	0.0048
b	3	.1694	423.0	30.9	−0.7	.1552	.0047

The calorimetric results of the reaction experiments of the second series are given in Table 5.

TABLE 5.—*Calorimetric results of the reaction experiments for hydrogen chloride, second series*

Experiment No.	ΔR	k	u	K	U	$\Delta t_{corr.}$	Average temperature
	Ohm	*Min*$^{-1}$	*Ohm Min*$^{-1}$	*Ohm*	*Ohm*	°*C.*	°*C.*
D	0.098361	0.001946	−0.0000012	0.002665	−0.000034	0.95034	30.00
E	.098986	.001968	−.0000030	.001771	−.000066	.96575	30.03
F	.089307	.002035	.0000022	.002792	.000062	.85825	30.00
G	.067365	.001927	.0000018	.002756	.000043	.64095	29.85
Mean							

Experiment No.	Electrical equivalent of calorimeter system	Total energy	"Gas" energy	"Spark" energy	Mass of HCl formed	$Q_{20°C.}$, 1 atmosphere	Deviation from mean
	Int. joules °*C.*$^{-1}$	*Int. joules*	*Joules*	*Joules*	*Mole*	*Int. joules mole*$^{-1}$	*Joules mole*$^{-1}$
D	15,415.3	14,649.8	38.5	10.3	0.159049	92,286	−22
E	15,433.8	14,905.2	19.7	10.3	.161479	92,363	+55
F	15,381.0	13,200.7	16.7	10.3	.143083	92,304	−4
G	15,406.4	9,874.8	16.8	10.3	.107079	92,280	−28
Mean						92,308	±27

4. RESULTS OF THE PRESENT INVESTIGATION

The results of the experiments of the present investigation are shown in Figure 3. This plot indicates clearly the increased precision obtained in the second series of reaction experiments and the relation of each result to the average value from the second series.

For the second series of reaction experiments the "error"

$$\pm 2\sqrt{\frac{(x-\bar{x})^2}{n(n-1)}}$$

is computed to be ±0.039 per cent. Combination [25] of this with the "error" of the electrical energy experiments gives a resultant error of 0.041 per cent, or ±38 joules per mole.

The total uncertainty in the average value of the second series is estimated to be not more than ±50 joules per mole.

The present experiments give, then, for the heat evolved in the reaction

$$1/2\ H_2\ (gas) + 1/2\ Cl_2\ (gas) = HCl\ (gas) \qquad (9)$$

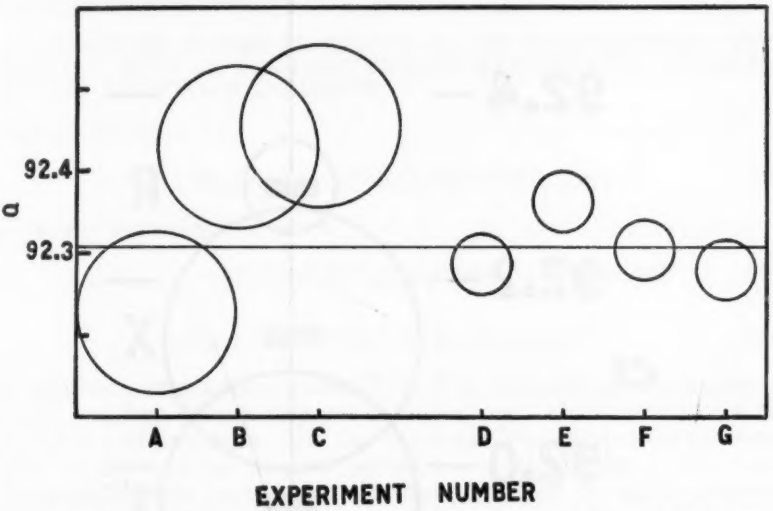

FIGURE 3.—*Plot of the experimental results for the heat of formation of gaseous HCl, from the present investigation*

The scale of ordinates gives Q, the heat of formation of gaseous HCl from its elements, at 30° C. and a constant pressure of 1 atmosphere, in international kilojoules mole^{-1}.
On the scale of abscissae are shown the individual values: A, B, C, the first series; and D, E, F, G, the second series. The circles indicate the relative precision for the two series, and the horizontal line, at 92.308, gives the average value from the second series.

at 30° C. and a constant pressure of 1 atmosphere

$$Q_{30°C.} = 92{,}308 \pm 50 \text{ international joules mole}^{-1} \qquad (10)$$

Since $\Delta C_p = -\frac{dQ}{dT} = -1.7$ joules mole^{-1} °C.$^{-1}$, the value for 25° C. and 1 atmosphere becomes

$$Q_{25°C.} = 92{,}300 \pm 50 \text{ international joules mole}^{-1} \qquad (11)$$

Using the factor 1.0004/4.185, this is equivalent to

$$Q_{25°C.} = 22{,}063 \pm 12 \text{ g-cal.}_{15} \text{ mole}^{-1}. \qquad (12)$$

5. THE RESULTS OF EARLIER INVESTIGATIONS

As has already been noted, calorimetric determinations of the heat of formation of hydrogen chloride have been made by Abria,[26] Favre and Silbermann,[27] Berthelot,[28] and Thomsen.[29] The results obtained

[25] See footnote 11, p. 681.
[26] See footnote 2, p. 680.
[27] See footnote 3, p. 680.
[28] See footnote 4, p. 680.
[29] See footnote 1, p. 680.

by Abria, and by Favre and Silbermann are, respectively, about 10 and 8 per cent higher than the values obtained by the later investigators, and may be disregarded in view of the more concordant work of later investigators who had the advantage of purer materials and better calorimetric technic. There are no details of Berthelot's experiments, though his value is practically identical with that of Thomsen.

Thomsen published complete details of his four experiments on hydrogen chloride. The writer has recomputed Thomsen's data in

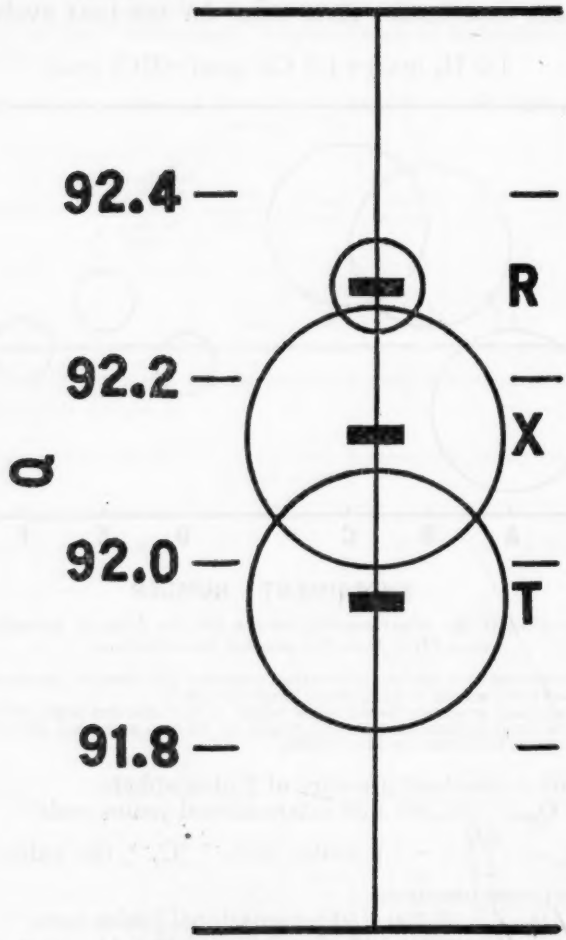

FIGURE 4.—*Plot of the various values for the heat of formation of* HCl

The scale of ordinates gives Q, the heat evolved in the formation of 1 mole of gaseous HCl from its elements, at 25° C. and a constant pressure of 1 atmosphere, in international kilojoules mole $^{-1}$.
The circles give the estimated uncertainties for values from the following sources: *T*, calorimetric experiments of Thomsen. X, calculation by way of the free energy and entropy of formation of gaseous HCl. *R*, calorimetric experiments of the present investigation.

the light of modern atomic weights and units of energy, and obtains as the average value

$$Q_{25°C.} = 91.96 \pm 0.14 \text{ international kilojoules mole}^{-1} \quad (13)$$

The "error" is estimated from the consistency of Thomsen's data, together with the assumption of a calibration error of 0.10 per cent. There still remains the possibility of there being an unknown systematic error in the above value.

The values from the various investigations are as follows, in international kilojoules per mole at 25° C. and 1 atmosphere:

Abria	101
Favre and Silbermann	99
Berthelot	92
Thomsen	91. 96 ± 0. 14
Present investigation	92. 30 ± 0. 05

In Figure 4, the value from Thomsen's data is shown in relation to the result obtained in the present investigation. The circles show the estimated uncertainties.

6. CORRELATION OF THE PRESENT DATA ON HEAT CONTENT WITH EXISTING DATA ON THE FREE ENERGY AND ENTROPY OF FORMATION OF HYDROGEN CHLORIDE

For the reaction

$$1/2\ H_2\ (gas) + 1/2\ Cl_2\ (gas) = HCl\ (gas) \qquad (14)$$

the present investigation gives

$$\Delta H_{298.1} = -92{,}300 \pm 50 \text{ international joules mole}^{-1} \qquad (15)$$

or

$$\Delta H_{298.1} = -22{,}063 \pm 12 \text{ g-cal.}_{15} \text{ mole}^{-1} \qquad (16)$$

The reference or standard state [30] used in calculating the values of entropy and free energy of a gas is that of an "ideal" gas where the fugacity is 1 atmosphere. In this state the heat content is the same as that of the real gas at zero pressure. A knowledge of the p-v-T relations suffices to permit computation of ΔH for the above reaction with the gases in their standard states by means of the relation

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p \qquad (17)$$

But the necessary P-V-T data for chlorine and hydrogen chloride are not available. A calculation employing the Berthelot equation of state, which requires only a knowledge of the critical temperature and pressure for each gas, shows that, although appreciable for chlorine and hydrogen chloride separately, the change in ΔH for reaction (14) from a pressure of 1 atmosphere to a fugacity of 1 atmosphere is only about 0.01 per cent of the value of ΔH. Without additional information this correction can for the present be neglected, as it is less than the uncertainty in the value of ΔH, and one can write

$$\Delta H^\circ_{298.1} = -22{,}063 \pm 12 \text{ g-cal.}_{15} \text{ mole}^{-1} \qquad (18)$$

The values of the entropies of hydrogen, chlorine, and hydrogen chloride (less the entropy of nuclear spin) have been calculated very accurately from the data of spectroscopy by Giauque,[31] and Giauque

[30] See footnote 5, p. 680. [31] Giauque, W. F., J. Am. Chem. Soc., vol. 52, p. 4816, 1930.

and Overstreet.[32] The values of $S°_{298.1}$, in g-cal.$_{15}$ mole^{-1} °C. $^{-1}$, are: H_2, 31.225; Cl_2, 53.310; HCl, 44.658. Then for reaction (14)

$$\Delta S°_{298.1} = 2.390 \text{ g-cal.}_{15} \text{ mole}^{-1} \text{ °C}^{-1} \quad (19)$$

For the present calculations the uncertainty in this value is negligible.

The value of $\Delta F°$ for reaction (14) is best obtained [33] by combining the data for the following reactions:

$$1/2\ H_2\ (\text{gas}) + \text{AgCl}\ (\text{solid}) = \text{HCl}\ (\text{aqueous}) + \text{Ag}\ (\text{solid}) \quad (20)$$

$$\text{Ag}\ (\text{solid}) + 1/2\ Cl_2\ (\text{gas}) = \text{AgCl}\ (\text{solid}) \quad (21)$$

$$\text{HCl}\ (\text{gas}) = \text{HCl}\ (\text{aqueous}) \quad (22)$$

The value for the free energy change in reaction (20) is obtained from the standard emf of the cell in which reaction (20) occurs. The best values are: [34] Randall and Young, 0.2221; Harned and Ehlers, 0.2224; Carmody, 0.2223; Spencer, 0.2222. These give

$$E°_{298.1} = 0.2222 \text{ international volt} \quad (23)$$

The uncertainty in this value is about 0.0002 volt. Then, for reaction (20)

$$\Delta F°_{298.1} = -5{,}125 \pm 5 \text{ g-cal.}_{15} \text{ mole}^{-1} \quad (24)$$

Randall and Young [35] conclude that the best value for the emf of the cell in which reaction (21) occurs is that given by Gerke [36] who finds, with chlorine at a pressure of 1 atmosphere,

$$E°_{298.1} = 1.1362 \text{ international volts} \quad (25)$$

Correcting the chlorine to a fugacity of 1 atmosphere,[37] one finds

$$E°_{298.1} = 1.1363 \text{ international volts} \quad (26)$$

The uncertainty in this value can be taken as 0.0004 volt. Therefore, for reaction (21)

$$\Delta F°_{298.1} = -26{,}211 \pm 9 \text{ g-cal.}_{15} \text{ mole}^{-1} \quad (27)$$

The value of $\Delta F°$ for reaction (22) can be calculated from the ratio of p_2, the vapor pressure of hydrogen chloride over its aqueous solution, to a_2, the activity of hydrogen chloride in that solution:

$$\Delta F° = -RT \ln \frac{p_2}{a_2} \quad (28)$$

Lewis and Randall [38] reviewed the data on the vapor pressure of

[32] Giauque, W. F., and Overstreet, R., J. Am. Chem. Soc., vol. 54, p. 1731, 1932.
[33] See footnote 7, p. 680.
[34] (*a*) See footnote 7, p. 680; (*b*) Harned, H. S., and Ehlers, R. W., J. Am. Chem. Soc., vol. 54, p. 1350, 1932; (*c*) Carmody, W. R., J. Am. Chem. Soc., vol. 54, p. 188, 1932; (*d*) Spencer, H. M., J. Am. Chem. Soc., vol. 54, p. 3647, 1932.
[35] See footnote 7, p. 680.
[36] Gerke, R. H., J. Am. Chem. Soc., vol. 44, p. 1684, 1922.
[37] See p. 499 of the reference given in footnote 5, p. 680.
[38] See p. 503 of the reference given in footnote 5, p. 680.

hydrogen chloride over its aqueous solution, and the activity of aqueous hydrogen chloride, and concluded that

$$\frac{p_2}{a_2}=4.41\times10^{-7} \tag{29}$$

Later, Randall and Young [39] recomputed this value, having available some few new data on vapor pressure and better values for a_2, and found

$$\frac{p_2}{a_2}=4.97\times10^{-7} \tag{30}$$

This value is 13 per cent higher than the previous one. Assuming the uncertainty in the latest value to be about 5 per cent, then, for reaction (22)

$$\Delta F^\circ_{298.1}=8{,}598\pm30 \text{ g-cal.}_{15} \text{ mole}^{-1} \tag{31}$$

Combination of ΔF° for reactions (20), (21), and (22), gives for reaction (14)

$$\Delta F^\circ_{298.1}=-22{,}738\pm33 \text{ g-cal.}_{15} \text{ mole}^{-1} \tag{32}$$

Then from equations (2), (19), and (32) one finds for reaction (14)

$$\Delta H^\circ_{298.1}=-22{,}026\pm33 \text{ g-cal.}_{15} \text{ mole}^{-1} \tag{33}$$

or

$$\Delta H^\circ_{298.1}=-92.14\pm0.14 \text{ international kilojoules mole}^{-1} \tag{34}$$

which agrees, within the limits of uncertainty, with the value obtained from the present calorimetric experiments

$$\Delta H^\circ_{298.1}=-92.30\pm0.05 \text{ international kilojoules mole}^{-1} \tag{35}$$

The values are shown together in Figure 4.

IV. CALCULATION OF SOME RELATED THERMODYNAMIC DATA

1. THE APPARENT AND PARTIAL MOLAL HEAT CAPACITY OF HYDROGEN CHLORIDE AND THE PARTIAL MOLAL HEAT CAPACITY OF WATER IN AQUEOUS SOLUTION OF HYDROGEN CHLORIDE

In order to calculate the temperature coefficient of reactions involving aqueous hydrogen chloride, it is necessary to know the apparent and partial molal heat capacities. The apparent molal heat capacity, Φ_c, is calculated from the experimental data on the heat capacity of hydrogen chloride solutions by the methods already described.[40]

When Φ_c has been determined as a function of $m^{1/2}$, the square root of the molality,[41] then $\overline{C}_{p_2}$, the partial molal heat capacity of hydrogen chloride, and $\overline{C}_{p_1}$, the partial molal heat capacity of water, are derived from the relations:

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[39] See footnote 7, p. 680.

[40] (a) Randall, M., and Rossini, F. D., J. Am. Chem. Soc., vol. 51, p. 323, 1929. (b) Rossini, F. D., B. S. Jour. Research, vol. 4, p. 313, 1930; (c) vol. 7, p. 47, 1931.

[41] m is the number of moles of solute per 1,000 g water.

$$\overline{C}_{p_2} = \Phi_c + 1/2m^{1/2}\frac{d\Phi_c}{dm^{1/2}} \tag{36}$$

$$\overline{C}_{p_2} - \overline{C}_{p_1} = -\frac{m}{55.508}\left(1/2m^{1/2}\frac{d\Phi_c}{dm^{1/2}}\right) \tag{37}$$

$$\Phi^\circ{}_c = \overline{C}_{p_2}{}^\circ \tag{38}$$

For the present compilation of the thermal data on aqueous hydrogen chloride, it is desired to obtain values of Φ_c over as large a range of concentration as possible. In a previous paper,[42] the present author reviewed the existing data from the dilute region of concentration to about 2 molal. To these data can be added the values for the more concentrated solutions and some new data for the dilute region.

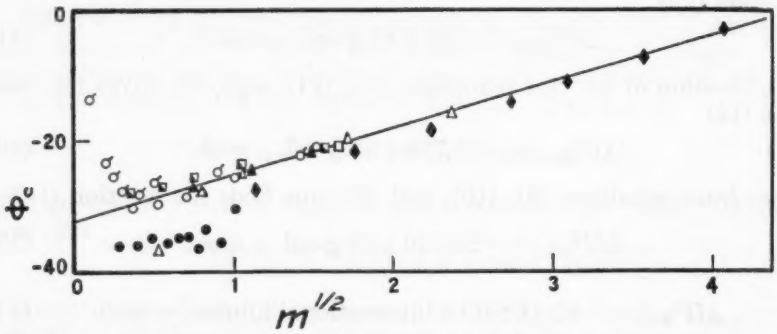

FIGURE 5.—*The apparent molal heat capacity of HCl in aqueous solution of HCl at 25° C.*

The scale of abscissae gives the square root of the molality.
The scale of ordinates gives Φ_c, the apparent molal heat capacity, for HCl in aqueous solution of HCl at 25° C., in g-cal. per mole.
The points designate values (corrected to 25° C.) from the data of the following investigators: ○Richards and Rowe; ◹Richards, Mair, and Hall; △Thomsen; □Thorvaldson, Brown, and Peaker; ◆Wrewsky and Savaritzky; ▲Marignac; ●Randall and Ramage; and, ◌Gucker and Schminke.

In Figure 5 are plotted values of Φ_c for aqueous hydrogen chloride at 25° C. calculated from the data of the following investigators: Thomsen [43] at 18° C.; Marignac [44] at 22° C.; Richards and Rowe [45] at 18° C.; Wrewsky and Kaigorodoff [46] at 20.5° C.; Randall and Ramage [47] at 25° C.; Richards, Mair, and Hall [48] at 18° C.; Thorvaldson, Brown, and Peaker [49] at 18° C.; Gucker and Schminke [50] at 25° C. The last-named investigators reported directly values of Φ_c. Where the data of the above experimenters were obtained at temperatures other than 25° C., they were corrected to 25° C., by means of the temperature coefficient of Φ_c previously given by the present author.[51]

The heavy black line in Figure 5 represents the linear relation between Φ_c and $m^{1/2}$ previously reported by the present author for aqueous hydrogen chloride at 25° C., for the range from infinite dilution to about 2 molal. Inspection of the plot shows that this relation

[42] See footnote 40 (c), p. 693.
[43] Thomsen, J., Ann. Physik, vol. 142, p. 337, 1871.
[44] Marignac, C., Ann. chim. phys., vol. 8, p. 410, 1876.
[45] Richards, T. W., and Rowe, A. S., J. Am. Chem. Soc., vol. 42, p. 162, 1920.
[46] Wrewsky, M., and Kaigorodoff, A., Z. physik, Chem., vol. 112, p. 83, 1924.
[47] Randall, M., and Ramage, L. E., J. Am. Chem. Soc., vol. 49, p. 93, 1927.
[48] Richards, T. W., Mair, B. J., and Hall, L. P., J. Am. Chem. Soc., vol. 51, p. 727, 1929.
[49] Thorvaldson, T., Brown, W. G., and Peaker, C. R., J. Am. Chem. Soc., vol. 52, p. 3927, 1930.
[50] Gucker, F. T., and Schminke, K. H., J. Am. Chem. Soc., vol. 54, p. 1358, 1932.
[51] See footnote 40 (c), p. 693.

represents the data very well over the entire range of concentration, though there is apparently some question as to the extrapolation to infinite dilution.[52]

Then for acqueous hydrogen chloride at 25°C.

$$\Phi_c = -32.5 + 7.2\ m^{1/2} \text{g-cal. mole}^{-1}\ ^\circ\text{C.}^{-1} \tag{39}$$

$$\overline{C}_{p_2} = -32.5 + 10.8\ m^{1/2} \text{g-cal. mole}^{-1}\ ^\circ\text{C.}^{-1} \tag{40}$$

$$\overline{C}_{p_1} - \overline{C}_{p_1}^\circ = -0.065\ m^{3/2} \text{g-cal. mole}^{-1}\ ^\circ\text{C.}^{-1} \tag{41}$$

The temperature coefficients of the above quantities can be taken as

$$\frac{d\Phi_c}{dT} = \frac{d\overline{C}_{p_2}}{dT} = \frac{2.0}{7} \text{ g-cal. mole}^{-1}\ ^\circ\text{C.}^{-2} \tag{42}$$

$$\frac{d(\overline{C}_{p_1} - \overline{C}_{p_1}^\circ)}{dT} = 0 \tag{43}$$

Equations (42) and (43) are approximations for the temperature range 10° to 35° C.

2. THE APPARENT AND PARTIAL MOLAL HEAT CONTENT OF HYDROGEN CHLORIDE AND THE PARTIAL MOLAL HEAT CONTENT OF WATER IN AQUEOUS SOLUTION OF HYDROGEN CHLORIDE AT 25° C.

In order to correlate the existing data on the heat of solution of hydrogen chloride and the heat of formation of aqueous hydrogen chloride with the present data on the heat of formation of gaseous hydrogen chloride, it is necessary to have values of $\Phi_h - \Phi_h^\circ$, the relative apparent molal heat content, for aqueous hydrogen chloride. These values can be easily determined from data on heat of dilution by the procedure previously employed by the present author.[53] The method consists simply in plotting the values of the measured heats of dilution as ordinates with the square root of the molality as the scale of abscissas. The intercept at $m^{1/2} = 0$ is made the zero for the scale of ordinates and the curve is then that of $\Phi_h - \Phi_h^\circ$ against $m^{1/2}$. Then the relative partial molal heat content of hydrogen chloride is obtained by means of the relation

$$H_2 - H_2^\circ = (\Phi_h - \Phi_h^\circ) + 1/2\ m^{1/2} \frac{d(\Phi_h - \Phi_h^\circ)}{dm^{1/2}} \tag{44}$$

and the relative partial molal heat content of water is given by

$$\overline{H}_1 - \overline{H}_1^\circ = -\frac{m}{55.508}\ 1/2\ m^{1/2} \frac{d(\Phi_h - \Phi_h^\circ)}{dm^{1/2}} \tag{45}$$

The existing data on heats of dilution (with the exception of many data for the dilute region of concentration which appeared in the paper already referred to [54]) are shown in Figure 6, where the ordi-

[52] Gucker, F. T., and Schminke, K. H. (see footnote 50, p. 694), found that, for aqueous hydrogen chloride and potassium hydroxide, the values of Φ_c at about 0.04 molal undergo an abrupt change, apparently increasing to very high values at infinite dilution. However, pending the confirmation of this behavior, which Gucker and Schminke found peculiar to hydrogen chloride and potassium hydroxide but not to lithium chloride, one can continue to use the linear extrapolation to infinite dilution.

[53] Rossini, F. D., B. S. Jour. Research, vol. 6, p. 791, 1931.

[54] See footnote 53, p. 695.

nate scale has already been shifted to make the plot one of $\Phi_h - \Phi_h^\circ$ against $m^{1/2}$. The values plotted in Figure 6 are from the data of Thomsen [55] at 18° C., Berthelot [56] at 18° C., and Wrewsky and Savaritzky [57] at 21.5° C. These data have been corrected to 25° C., using the appropriate values for heat capacity. The curve in the region from $m^{1/2}=0$ to $m^{1/2}=1.4$ represents values of $\Phi_h - \Phi_h^\circ$ for 25° C., calculated from those for $\Phi_h - \Phi_h^\circ$ at 18° C. which have already been compiled by the present author.[58]

In the above manner the values given in Tables 6 and 7 have been derived. Table 6 gives $\Phi_h - \Phi_h^\circ$ for aqueous hydrogen chloride

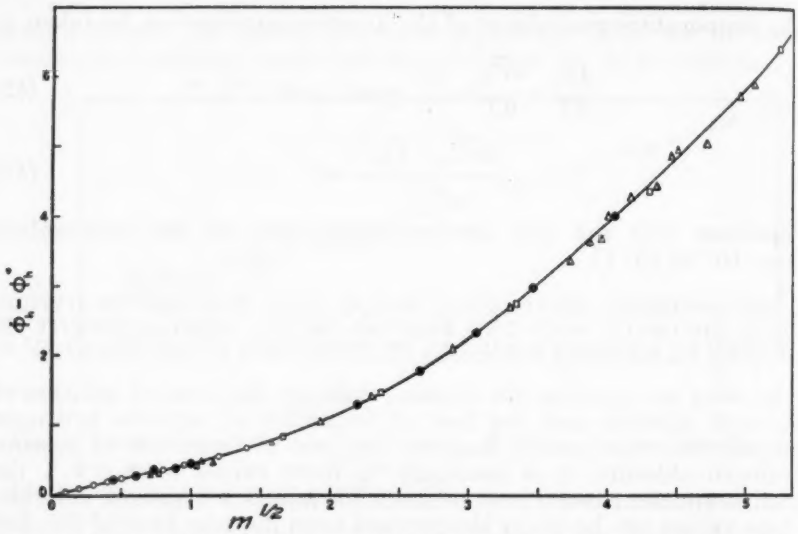

FIGURE 6.—*The relative apparent molal heat content of HCl in aqueous solution of HCl at 25° C.*

The scale of abscissas gives the square root of the molality.
The scale of ordinates gives $\Phi_h - \Phi_h^\circ$, the relative apparent molal heat content, for HCl in aqueous solution of HCl at 25° C., in kg-cal.$_{15}$ per mole.
The points designate the experimental values (corrected to 25° C.) of the following investigators: ●, Wrewsky and Savaritzky; △, Berthelot; and □, Thomsen.
The points marked ○ are values (corrected to 25° C.) obtained from those for 18° C. previously given by the present author.

at 25° C., with the composition of the solution expressed in terms of the number of moles of water associated with 1 mole of hydrogen chloride. Table 7 gives values for $\Phi_h - \Phi_h^\circ$, $\overline{H}_2 - \overline{H}_2^\circ$, and $\overline{H}_1 - \overline{H}_1^\circ$, at 25° C., for selected values of $m^{1/2}$.

[55] Thomsen, J., Thermochemische Untersuchungen, vol. 2, Barth, Leipzig, 1886.
[56] Berthelot, M., Ann. chim. phys., vol. 4, p. 467, 1875.
[57] Wrewsky, M., and Savaritzky, N., Z. physik. Chem., vol. 112, p. 90, 1924.
[58] See footnote 53, p. 695.

TABLE 6.—*Relative apparent molal heat content of HCl in aqueous solution of HCl, at 25° C.*

[The composition of the solution is given in terms of the number of moles of H_2O associated with 1 mole of HCl]

Solution	$\Phi_A-\Phi_A^\circ$	Solution	$\Phi_A-\Phi_A^\circ$
	g-cal per mole of HCl		*g-cal per mole of HCl*
$HCl.\infty H_2O$	0	$HCl.18H_2O$	920
$HCl.6400H_2O$	46	$HCl.15H_2O$	1,050
$HCl.3200H_2O$	65	$HCl.12H_2O$	1,250
$HCl.1600H_2O$	90	$HCl.10H_2O$	1,460
$HCl.800H_2O$	128	$HCl.8H_2O$	1,760
$HCl.400H_2O$	181	$HCl.6H_2O$	2,320
$HCl.200H_2O$	249	$HCl.5H_2O$	2,760
$HCl.100H_2O$	343	$HCl.4H_2O$	3,440
$HCl.50H_2O$	483	$HCl.3H_2O$	4,480
$HCl.25H_2O$	730	$HCl.2H_2O$	6,400
$HCl.20H_2O$	850	$HCl.1H_2O$	11,800

TABLE 7.—*Apparent and partial molal heat content of HCl and partial molal heat content of H_2O in aqueous solution of HCl, at 25° C.*

$m^{1/2}$	m moles of HCl per 1,000 g H_2O	$\Phi_A-\Phi_A^\circ$ g-cal. per mole of HCl	$\overline{H}_2-\overline{H}_2^\circ$ g-cal. per mole of HCl	$\overline{H}_1-\overline{H}_1^\circ$ g-cal. per mole of H_2O
0	0	0	0	0
.1	.01	49	74	−.0045
.2	.04	98	146	−.0346
.3	.09	146	219	−.119
.4	.16	193	287	−.271
.5	.25	238	348	−.496
.6	.36	281	412	−.850
.8	.64	367	543	−2.03
1.0	1.00	458	700	−4.35
1.2	1.44	561	884	−8.35
1.4	1.96	675	1,095	−14.8
1.6	2.56	805	1,350	−25.3
1.8	3.24	955	1,650	−40.9
2.0	4.00	1,120	2,000	−63.4
2.5	6.25	1,610	3,040	−161
3.0	9.00	2,260	4,410	−349
3.5	12.25	3,040	5,960	−644
4.0	16.00	3,920	7,560	−1,040
4.5	20.25	4,860	9,170	−1,570
5.0	25.00	5,840	10,840	−2,250
5.5	30.25	6,860		

3. THE HEAT OF SOLUTION OF HYDROGEN CHLORIDE IN WATER

The heat of solution of hydrogen chloride in water has been measured by Thomsen,[59] Berthelot and Louguinine,[60] and Wrewsky and Savaritzky.[61] The data of these investigators have been corrected to 25° C. by means of the proper values of heat capacity and are shown in Figure 7. These data are for the reaction

$$HCl\ (gas)+\frac{55.508}{m}\ H_2O\ (liquid)=HCl\cdot\frac{55.508}{m}H_2O\ (solution) \quad (46)$$

[59] Thomsen, J., Thermochemische Untersuchungen, vol. 2, Barth, Leipzig, 1886.
[60] Berthelot, M., and Louguinine, W., Ann. chim. phys., vol. 6, p. 289, 1875.
[61] See footnote 57, p. 696.

The curve shown in Figure 7 is drawn through the data of Wrewsky and Savaritzky with extrapolation to infinite dilution made with the aid of the values of $\Phi_h - \Phi_h^\circ$ given in Table 7.

From these data the value for the heat of solution of hydrogen chloride at infinite dilution in water at 25° C.

$$HCl\ (gas) = HCl\ (aqueous,\ m=0) \tag{47}$$

is

$$\Delta H^\circ_{298.1} = -17{,}880 \pm 40\ \text{g-cal.}_{15}\ \text{mole}^{-1} \tag{48}$$

4. THE HEATS OF FORMATION OF SILVER CHLORIDE AND MERCUROUS CHLORIDE

In order to utilize the data on the temperature coefficient of the emf of certain cells for obtaining the heat of formation of aqueous

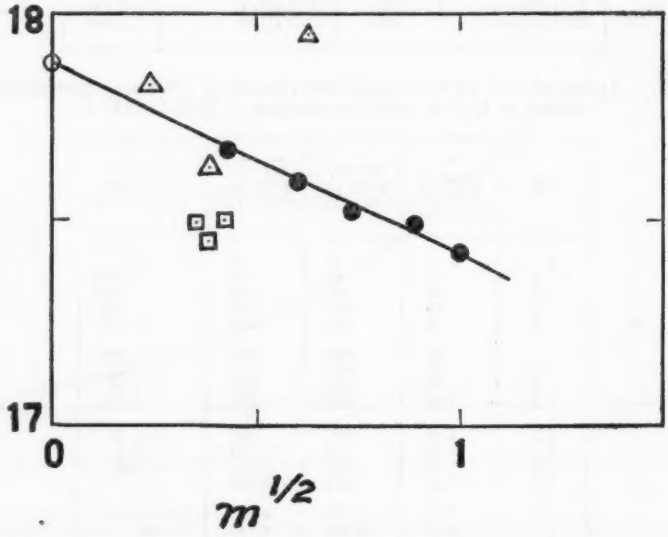

FIGURE 7.—*The heat of solution of HCl (gas) in water at 25° C.*

The scale of abscissae gives the square root of the molality.

The scale of ordinates gives the heat of the reaction $HCl_{(gas)} + \frac{55.508}{m} H_2O_{(liquid)} = HCl \cdot \frac{55.508}{m} H_2O_{(solution)}$ at 25° C., in kg-cal.$_{15}$ per mole of HCl.

The points designate the experimental values (corrected to 25° C.) of the following investigators: ●, Wrewsky and Savaritzky; △, Berthelot and Longuinine; and □, Thomsen.

The point marked ○, at $m^{1/2}=0$, gives the value for infinite dilution.

hydrogen chloride, it is necessary to have accurate values for the heats of formation of silver chloride and mercurous chloride. Fortunately, data are available for calculating these values with considerable accuracy.

For the reaction

$$Ag\ (solid) + 1/2\ Cl_2\ (gas) = AgCl\ (solid) \tag{49}$$

the free energy change [62] is

$$\Delta F^\circ_{298.1} = -26{,}211 \pm 9\ \text{g-cal.}_{15}\ \text{mole}^{-1} \tag{50}$$

The entropy change for reaction (49) can be calculated from two independent sources: (1) From values of the entropies of silver,

[62] See p. 692. The difference in free energy between crystalline and chemically precipitated silver chloride was found by Randall and Young (see footnote 7, p. 680) to be zero within the limits of uncertainty.

chlorine, and silver chloride; and (2) from a knowledge of the temperature coefficient of the emf of the cell in which reaction (49) occurs. New data on the heat capacity of silver and silver chloride down to low temperatures have been obtained recently. From such measurements, Eucken, Clusius, and Woitinek [63] obtained for silver, $S°_{298.1} = 10.16$; Giauque and Meads [64] reported a preliminary value for silver, $S°_{298.1} = 10.01$; and Eastman and Milner [65] gave for crystalline silver chloride $S°_{298.1} = 22.97 \pm 0.08$. The entropy of silver will be taken as 10.09 ± 0.07. Combining these data with those of Giauque and Overstreet [66] on chlorine one finds for reaction (49)

$$\Delta S°_{298.1} = -13.77 \pm 0.12 \text{ g-cal.}_{15} \text{ mole}^{-1} \quad (51)$$

For the temperature coefficient of the emf of the cell in which reaction (49), with chemically precipitated silver chloride, occurs, Gerke [67] found for 25° C., the value

$$\frac{dE}{dT} = -0.000595 \pm 0.000006 \text{ international volt } ° \text{C}^{-1}$$

Correcting the chlorine to unit fugacity, one obtains for reaction (49)

$$\Delta S°_{298.1} = -13.69 \pm 0.14 \text{ g-cal.}_{15} \text{ mole}^{-1} ° \text{ C.}^{-1} \quad (52)$$

The average of (51) and (52) gives for reaction (49)

$$\Delta S°_{298.1} = -13.73 \pm 0.12 \text{ g-cal.}_{15} \text{ mole}^{-1} ° \text{ C.}^{-1} \quad (53)$$

By means of equations (2), (50), and (53) one finds for reaction (49)

$$\Delta H°_{298.1} = -30{,}304 \pm 40 \text{ g-cal.}_{15} \text{ mole}^{-1} \quad (54)$$

Within the limits of uncertainty this value is apparently that for either crystalline or chemically precipitated silver chloride.

For calculating the heat of formation of mercurous chloride, a slightly different procedure is necessary because an accurate value for the entropy of mercurous chloride is not available.

For the cell in which the reaction was

$$\text{Ag (solid)} + \text{HgCl (solid)} = \text{AgCl (solid)} + \text{Hg (liquid)} \quad (55)$$

Gerke [68] found, at 25° C., with chemically precipitated salts

$$\frac{dE}{dT} = 0.000338 \pm 0.000002 \text{ international volt } °C.^{-1} \quad (56)$$

and

$$E°_{298.1} = 0.0455 \text{ international volt} \quad (57)$$

This latter value is well substantiated [69] by measurements of other investigators, and the uncertainty can be taken as ± 0.0003 volts.

Using the Gibbs-Helmholtz relation

$$\Delta H = NF\left(T\frac{dE}{dT} - E\right) \quad (58)$$

one finds for reaction (55)

$$\Delta H°_{298.1} = 1276 \pm 16 \text{ g-cal.}_{15} \text{ mole}^{-1} \quad (59)$$

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[63] Eucken, A., Clusius, K., and Woitinek, H., Z. anorg. Chem., vol. 203, p. 39, 1931.
[64] Giauque, W. F., and Meads, P. F., see footnote 6, p. 680.
[65] Eastman, E. D., and Milner, R. T., personal communication.
[66] See footnote 6, p. 680.
[67] See footnote 36, p. 692.
[68] See footnote 36, p. 692.
[69] See footnote 7, p. 680.

Combination of reactions (49) and (55) gives

$$\text{Hg (liquid)} + 1/2\ \text{Cl}_2\ \text{(gas)} = \text{HgCl (solid)} \quad (60)$$

for which

$$\Delta H^\circ_{298.1} = -31{,}580 \pm 45\ \text{g-cal.}_{15}\ \text{mole}^{-1} \quad (61)$$

5. THE HEAT OF FORMATION OF AQUEOUS HYDROGEN CHLORIDE

It is possible to obtain a fairly accurate value for the heat of formation of hydrogen chloride in aqueous solution from data on the temperature coefficient of certain cells and the heats of formation of silver chloride and mercurous chloride.

Lewis and Randall,[70] Ellis,[71] and Harned and Brumbaugh [72] measured at a series of temperatures the emf of cells in which the reaction was

$$1/2\ \text{H}_2\ \text{(gas)} + \text{HgCl (solid)} = \text{Hg (liquid)} + \text{HCl (aqueous, } m\text{)} \quad (62)$$

and from these data calculated, by the Gibbs-Helmholtz relation, ΔH for reaction (62). By adding to (62) the reaction for the formation of mercurous chloride (solid) one obtains

$$1/2\ \text{H}_2\ \text{(gas)} + 1/2\ \text{Cl}_2\ \text{(gas)} = \text{HCl (aqueous, } m\text{)} \quad (63)$$

In an analogous manner one can combine the data of Noyes and Ellis,[73] Harned and Brumbaugh,[74] and Butler and Robertson [75] on cells in which the reaction was

$$1/2\ \text{H}_2\ \text{(gas)} + \text{AgCl (solid)} = \text{Ag (solid)} + \text{HCl (aqueous, } m\text{)} \quad (64)$$

with the heat of formation of silver chloride to obtain the heat of formation of aqueous hydrogen chloride.

These data give the heat of formation of 1 mole of hydrogen chloride in an infinite amount of aqueous solution of hydrogen chloride of molality m. To the various values of ΔH for reaction (62) have been added the appropriate values of $\overline{H}_2 - \overline{H}_2^\circ$, taken from Table 7, in order to obtain the heat of the reaction

$$1/2\ \text{H}_2\ \text{(gas)} + \text{HgCl (solid)} = \text{Hg (liquid)} + \text{HCl (aqueous, } m = 0\text{)} \quad (65)$$

In this manner the following values for reaction (65) were obtained:

Data from—	Number of different molalities	Range of molality	$\Delta H^\circ_{298.1}$
Lewis and Randall	1	0.1	−8,429
Ellis	8	4.484–0.0333	−8,370
Harned and Brumbaugh	1	0.1	−8,400

The average of these values is −8,400, exactly the value of the latest determination, and the uncertainty can be taken as ±30. Combination of reactions (60) and (65) gives

$$1/2\ \text{H}_2\ \text{(gas)} + 1/2\ \text{Cl}_2\ \text{(gas)} = \text{HCl (aqueous, } m = 0\text{)} \quad (66)$$

for which

$$\Delta H^\circ_{298.1} = -39{,}980 \pm 55\ \text{g-cal.}_{15}\ \text{mole}^{-1} \quad (67)$$

[70] Lewis, G. N., and Randall, M., J. Am. Chem. Soc., vol. 36, p. 1969, 1914.
[71] Ellis, J. H., J. Am. Chem. Soc., vol. 38, p. 737, 1916.
[72] Harned, H. S., and Brumbaugh, N. J., J. Am. Chem. Soc., vol. 44, p. 2729, 1922.
[73] Noyes, A. A., and Ellis, J. H., J. Am. Chem. Soc., vol. 39, p. 2532, 1917.
[74] See footnote 72, p. 700.
[75] Butler, J. A. V., and Robertson, C. M., Proc. Roy. Soc. (London), vol. 125, p. 694, 1929.

In like manner, adding the appropriate values of $\overline{H}_2 - \overline{H}_2°$ to convert the data to infinite dilution, one finds for the reaction

$$1/2\ H_2\ (\text{gas}) + \text{AgCl (solid)} = \text{Ag (solid)} + \text{HCl (aqueous, } m = 0) \quad (68)$$

the following values:

Data from—	Number of molalities	Range of molality	$\Delta H°_{298.1}$
Noyes and Ellis	6	0.1–0.001	−9,552
	1	0.33314	−9,643
Harned and Brumbaugh	1	0.01	−9,611
	1	0.00	−9,567
Butler and Robertson	4	0.1–0.01	−9,554
	1	0.3	−9,638

Taking the average of these values, one finds for reaction (68)

$$\Delta H°_{298.1} = -9{,}594 \pm 50\ \text{g-cal.}_{15}\ \text{mole}^{-1} \quad (69)$$

Combination of equations (54) and (69) gives for reaction (66)

$$\Delta H°_{298.1} = -39{,}898 \pm 65\ \text{g-cal.}_{15}\ \text{mole}^{-1} \quad (70)$$

Taking the average of (67) and (70) one finds for reaction (66)

$$\Delta H°_{298.1} = -39{,}938 \pm 55\ \text{g-cal.}_{15}\ \text{mole}^{-1} \quad (71)$$

This value, fortunately, is practically identical with that obtained by combining equations (18) and (48) which give for reaction (66)

$$\Delta H°_{298.1} = -39{,}943 \pm 40\ \text{g-cal.}_{15}\ \text{mole}^{-1} \quad (72)$$

which will be taken as the best value for the heat of formation of aqueous hydrogen chloride at infinite dilution.

6. THE FREE ENERGY OF FORMATION OF GASEOUS HYDROGEN CHLORIDE

The free energy of formation of gaseous hydrogen chloride is given by equation (32) as

$$\Delta F°_{298.1} = -22{,}738 \pm 33\ \text{g-cal.}_{15}\ \text{mole}^{-1} \quad (32)$$

A value having a smaller uncertainty than the foregoing one can be calculated from equations (2), (18), and (19). This gives

$$\Delta F°_{298.1} = -22{,}775 \pm 12\ \text{g-cal.}_{15}\ \text{mole}^{-1} \quad (73)$$

7. THE ENTROPY OF AQUEOUS HYDROGEN CHLORIDE

The entropy of aqueous hydrogen chloride is the basis for the calculation of the entropies of aqueous ions according to the methods of Latimer and coworkers.[76]

For the reaction

$$1/2H_2\ (\text{gas}) + 1/2Cl_2\ (\text{gas}) = \text{HCl (aqueous)} \quad (74)$$

one finds by combining equations (2), (24), (27), and (72)

$$\Delta S°_{298.1} = -28.87 \pm 0.15\ \text{g-cal.}_{15}\ \text{mole}^{-1}\ °\text{C.}^{-1} \quad (75)$$

[76] See footnote 8, p. 681.

Then for aqueous hydrogen chloride at hypothetical 1 molal, where its heat content is the same as that at infinite dilution,

$$S^{\circ}_{298\cdot1} = 13.40 \pm 0.15 \text{ g-cal.}_{15} \text{ mole}^{-1} {}^{\circ}\text{C.}^{-1} \quad (76)$$

V. ACKNOWLEDGMENT

The author acknowledges the technical advice of E. W. Washburn, under whose direction this work was carried on.

WASHINGTON, September 14, 1932.

THERMAL EXPANSION OF LEAD

By Peter Hidnert and W. T. Sweeney

ABSTRACT

Measurements have been made on the linear thermal expansion of three samples of cast lead between room temperature and 300° C. and the results have been correlated with data obtained by other investigators between 1740 and 1931.

A curve has been derived which shows the linear thermal expansion of lead between −253° and +300° C. The summary gives average coefficients of expansion for various temperature ranges between −250° and +300° C.

A comparison of the indirect results by Kopp and Matthiessen with the direct data by other observers, indicates that lead expands the same in all directions.

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I. INTRODUCTION

The thermal expansion of lead has been of considerable interest for nearly 200 years. Its measurement has been the object of more than 25 investigations. A summary of available data obtained by various investigators is given in Table 1.

Between 1740 and 1831, a number of determinations of the coefficient of linear expansion were made for the range from 0° to 100° C. In 1831, Daniell reported the changes in length of a bar of lead heated from 17° to 100° C. and to the point of fusion, respectively. From that time up to 1930, no measurements on the linear thermal expansion of lead above 110° C. have been located in the literature. The present authors appear to have been the first observers after Daniell to report data on the linear thermal expansion of lead above 110° C. Their abstract giving coefficients of linear expansion on heating for various temperature ranges between 20° and 300° C. was published [1] in February, 1930. In October of the same year, Uffelmann [2] published coefficients of linear expansion for various temperatures between 80° and 280° C.

The present investigation was undertaken in order to obtain reliable data on the linear thermal expansion of lead above 100° C. The data obtained between 20° and 300° C. have been correlated with results by other observers.

The authors wish to express appreciation to H. W. Bearce, W. Souder, and H. S. Rawdon for valuable suggestions, and to H. S. Krider for assistance during the preparation of the manuscript.

[1] Hidnert and Sweeney. (See Table 1.)
[2] See Table 1.

TABLE 1.—*Summary of expansion data on lead by various observers*

Observers	Date	Reference	Material	Temperature or temperature range	Coefficient of linear expansion per °C.	Remarks
				°C.	$\times 10^{-6}$	
Muschembroeck [1]	1740 (?)		Lead	0 to 100	14.2	
Bouguer	1745	Hist. Acad. Roy. Sci., p. 230, 1745	do	0 to 100	10.9	
Ellicot [1]	Before 1754		do	0 to 100	28.5	
Smeaton	1754	Phil. Trans., vol. 48, pt. 2, p. 598, 1754	do	0 to 100	28.7	
Herbert [1]	Before 1779		do	0 to 100	26.2	
Berthoud [1]	Before 1808		do	0 to 100	34.5	
Guyton	1811	Mém. Sci. Math. Phys. Inst. Imp. France, 2d pt., p. 89, 1811.	do	0 to 100	27.2	
Lavoisier and Laplace [2]	Before 1831		do	0 to 100	28.5	
Daniell	1831	Phil. Trans., vol. 121 (pt. 1), p. 443, 1831, or Phil. Mag., series 3, vol. 1, pp. 197, 261, 1832.	do	17 to 100	27.9	Computed in 1932 from data by Daniell.
				17 to 327	29.3	
Kopp	1852	Ann. Chem. Pharm., vol. 81, p. 1, 1852	Lead, cast	14 to 99	29.9	Coefficients of linear expansion were computed by Kopp from coefficients of cubical expansion obtained by density method
				15 to 99	27.8	
				11 to 42	31.2	
Calvert, Johnson, and Lowe	1859	Rep. Brit. Assoc., vol. 28, p. 46, 1859; Proc. Roy. Soc. (London), vol. 10, p. 315, 1859–60 and Chem. News. vol. 3, pp. 315, 357, 371, 1861.	Lead (pure)	0 to 100	30.1	
Matthiessen	1866	Phil. Trans., vol. 156, p. 861, 1866; or Ann. Physik u. Chemie, vol. 130, p. 50, 1867.	Lead, cast in a well-smoked mold and varnished.	14 to 92	[3] 28.0	$L_t = L_0(1+10^{-4}\times 0.2726t+10^{-6}\times 0.0074t^2)$, computed by Matthiessen from his data on cubical expansion obtained by weighing 2 samples of lead in water at different temperatures.
Fizeau	1869	Compt. Rend., vol. 68, p. 1125, 1869 or Ann. Physik u. Chemie, vol. 138, p. 26, 1869.	Lead, cast	40	29.2	
				0 to 100	29.5	
Buff	1872	Ann. Physik u. Chemie, vol. 145, p. 626, 1872	Lead	0 to 100	28.5	Computed in 1932 from coefficient of cubical expansion reported by Buff.
Pfaff	1872	(Erlangen. Besold. 1872. 8° 1–20), Fortsch. Physik, vol. 29, p. 579, 1873.	Lead wire	0 to 100	29.1	
Glatzel	1877	Ann. Physik u. Chemie, vol. 160, p. 497, 1877	Lead rod made from drawn wire.	Room temperature to 100. (?)	29.4	
Rodwell	1877	Proc. Roy. Soc. (London), vol. 25, p. 280, 1876–77.	Lead		30.2	
Vicentini and Omodei	1888	Atti Accad. Sci. Torino, vol. 23, p. 38, 1887–88.	do	325	29.5	Computed in 1932 from coefficient of cubical expansion reported by Vicentini and Omodei.
Dorsey	1908	Phys. Rev., vol. 27, p. 1, 1908	Lead, cast	−160	24.8	
				−120	25.9	
				−80	27.2	
				−40	28.5	
				0	28.9	
				−180 to +20	27.1	

Dorsey	1908	Phys. Rev., vol. 27, p. 1, 1908	Lead, cast	−80	27.2	
				−40	28.5	
				0	28.9	
				−180 to +20	27.1	
Grüneisen	1910	Ann. Physik, vol. 33, p. 33, 1910	Lead rod	−190 to +17	27.0	
				+17 to 100	29.3	
				18	28.8	
Lindemann	1911	Physik. Z., vol. 12, p. 1197, 1911	Lead, chemically pure.	−253 to −192	19.8	Determined expansion of lead by comparison with expansion of fused quartz. Lindemann states that he neglected the expansion of the latter for it is extremely small and within the experimental error.
				−190 to −183	20.3	
				−190 to +20	26.6	
Rauramo and Saarialho	1912	Öfversigt Finska Vetenskaps-Soc. Fördh., vol. 54, 1911-12, Afd. A., N:o 24.	Lead, cast	+15 to 110	29.3	
Friend and Vallance	1924	J. Inst. Metals, vol. 31, p. 75, 1924	Lead	10 to 100	29.5	
Ebert	1928	Z. Physik, vol. 47, p. 712, 1928	do	−253 to 0	24.7	Computed in 1932 from the data reported by Ebert.
				−190 to 0	26.1	
				−253 to −190	20.8	
				0 to +100	28.9	
Hidnert and Sweeney	1930	Phys. Rev., vol. 35, p. 296, 1930	Lead, cast	20 to 60	28.8	Average values obtained on 3 samples from observations on heating.
				20 to 100	29.0	
				20 to 200	30.0	
				20 to 300	31.4	
Uffelmann	1930	Phil. Mag., vol. 10, p. 633, 1930	Lead, annealed	80	28.9	
				100	29.1	
				120	29.5	
				140	29.9	
				160	30.2	
				170	30.3	
				180	30.5	
				190	30.9	
				200	31.2	
				220	31.6	
				240	32.0	
				250	32.3	
				260	32.0	
				280	34.3	
McLennan, Allen, and Wilhelm.	1931	Trans. Roy. Soc. Can., III, series 3, vol. 25, p. 1, 1931.	Lead	−268 to −246	-------	Determined relative expansion of lead and fused quartz; the curve of the relative change of length is nearly horizontal in the region of the superconductivity point of lead (−266° C.). The authors state that as there was no discontinuity observed in the thermal expansion curve for lead, it seems fair to conclude that when with the lowering temperatures the superconductivity point was passed, no sudden change in the crystal lattice of the metal accompanied the appearance of superconductivity.

[1] Cited by Guyton de Morveau (Mém. Sci. Math. Phys. Inst. France, second semestre, p. 1, 1808).
[2] Cited by Daniell (Phil. Mag., vol. 10, pp. 191, 268, 350, 1831).
[3] Computed in 1932 from Matthiessen's equation.

II. MATERIALS INVESTIGATED

Three samples of cast lead were investigated. The purity and the method of casting of the samples are indicated in Table 2. The length of each sample was about 300 mm and the cross section 10 mm square.

III. APPARATUS

The furnace shown in Figure 1 of Scientific Paper of the Bureau of Standards No. 488, was used for the measurements of the linear thermal expansion of sample 1001 and the white furnace shown at the extreme left of Figure 1 of Scientific Paper of the Bureau of Standards No. 524 was used for samples 1144 and 1215. Figure 4 of the latter paper indicates the method used in mounting samples 1144 and 1215 in the furnace.

Expansion measurements were made by means of micrometer microscopes, which were sighted on fine wires suspended from or in contact with the ends of the specimen. For a detailed description of the apparatus and the methods used the reader should refer to the publications mentioned.

IV. RESULTS

Observations were made on the linear thermal expansion of three cast samples of lead at various temperatures between room temperature and 300° C. and the results obtained are shown in Figure 1. The expansion curves are plotted from different origins to display the individual characteristics of each curve.

The average coefficients of expansion given in Table 2 were derived from the observations on heating and on cooling. This table also gives the differences in length before and after the expansion tests. The plus (+) sign indicates an increase in length and the minus (−) sign a decrease in length.

TABLE 2.—*Average coefficients of linear expansion of cast lead*

Sample	Lead content[1]	Method of casting	Test No.	Heating or cooling	Average coefficients of expansion per ° C.				Change in length after heating to 300° C. and cooling to room temperature
					20° to 60° C.	20° to 100° C.	20° to 200° C.	20° to 300° C.	
	Per cent				×10⁻⁶	×10⁻⁶	×10⁻⁶	×10⁻⁶	*Per cent*
[2] 1001	-------	Preheated steel mold	1	Heating	29.2	29.6	31.2	32.5	+0.02
				Cooling	------	29.3	30.4	31.6	
[2] 1144	99.9	Sand mold	1	Heating	28.3	28.6	29.5	31.2	.00
				Cooling	------	29.5	------	31.2	
[2] 1215	99.8	Sand mold, from same ingot as sample 1001.	1	Heating	29.0	28.9	29.7	30.9	−.01
				Cooling	------	28.8	------	31.1	
			2	Heating	------	28.8	29.4	31.0	.00
				Cooling	------	------	29.8	31.0	
		Average	------	------	28.8	29.1	30.0	31.3	------

[1] Analysis by H. A. Buchheit, of this bureau.
[2] See sample 1215.
[3] Density for samples 1144 and 1215, 11.310 and 11.329 g/cm³ at 25° C., respectively, determined by Miss E. E. Hill, of this bureau.

The differences obtained in the coefficients of expansion of the three samples of cast lead are probably due to variations in the methods of casting.

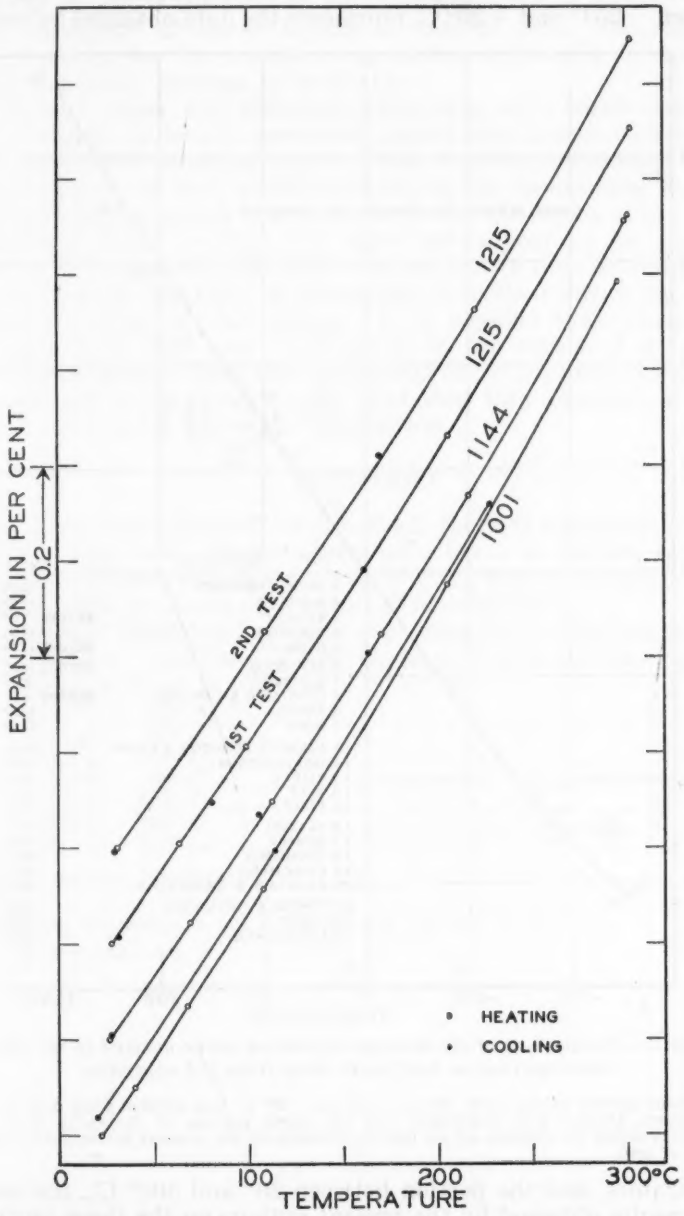

FIGURE 1.—*Linear thermal expansion of three cast samples of lead*

Sample 1001 which was cast in a preheated steel mold, has larger coefficients of expansion than the samples cast in sand molds. From the observations obtained on cooling, it appears that the coefficients

of expansion of sample 1001 on the next heating would be less than those obtained on the first heating.

The curve in Figure 2 represents the linear thermal expansion of lead between −253° and +300° C. The portion of the curve between −253° and +20° C. represents the data obtained by previous

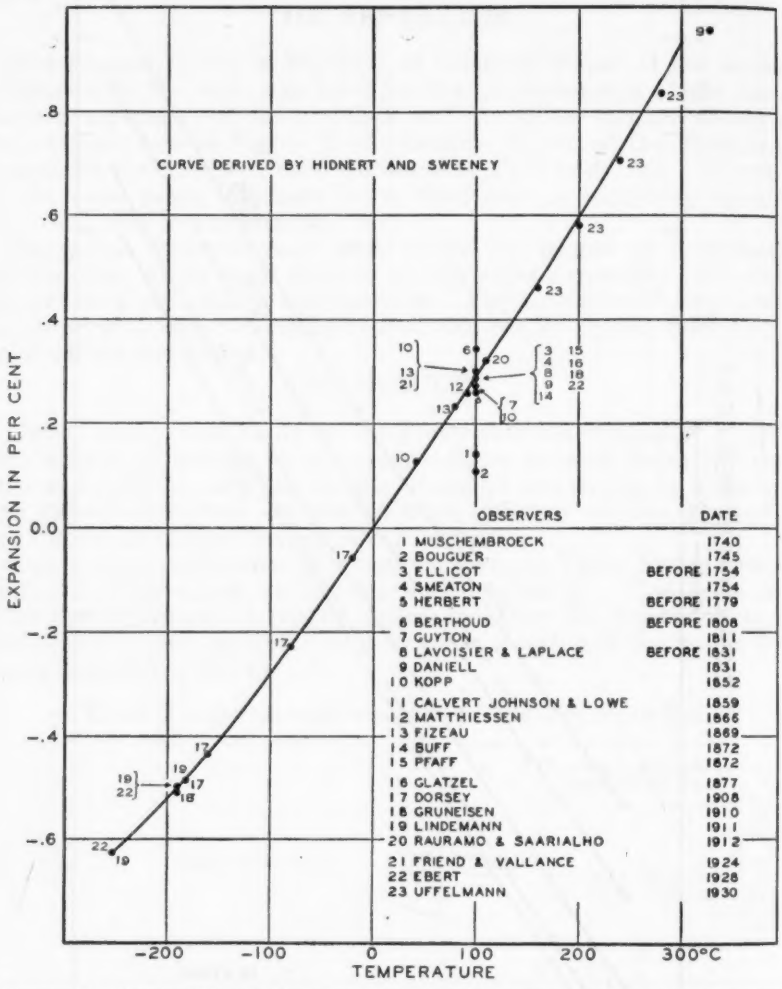

FIGURE 2.—*Comparison of the average expansion curve derived in the present investigation on lead, with data from the observers*

The lower portion of the curve from −253° to +20° C. was derived from data by Lindemann, Ebert, Dorsey, and Grüneisen, and the upper portion of the curve from 20° to 300° C. represents the average of all results obtained in the present investigation on three samples of lead.

investigators, and the portion between 20° and 300° C., the average of all results obtained by the present authors on the three samples of lead. The values obtained by other observers are included in this figure for comparison. Most of these values show good agreement. Bouguer and Muschembroeck obtained the lowest values and Berthoud the highest value at 100° C.

Kopp and Matthiessen's data for linear expansion obtained indirectly from density measurements agree closely with direct measurements made by other observers, and therefore it appears that the expansion of lead is the same in all directions.

The coefficient of linear expansion derived from Vicentini and Omodei's value for the coefficient of cubical expansion of lead near the melting point, appears to be too low.

McLennan, Allen, and Wilhelm published a curve which shows the relative change of length measured against the change of length of fused quartz near absolute zero. Their conclusion relating to the lattice structure of lead, which is based on the assumption that the expansion curve of lead is almost horizontal in the region of the superconductivity point (−266° C.), does not appear to be justified. Since the expansion of fused quartz is not known near absolute zero, it is not possible definitely to determine from their curve the actual expansion of lead in this region. It is possible that when these observers cooled lead and fused quartz in the region of the superconductivity point of lead, the contraction of the lead nearly balanced the expansion of the fused quartz [3] and thus they obtained a nearly horizontal curve for the relative expansion.

V. SUMMARY

Data have been obtained on the linear thermal expansion of three samples of cast lead. Observations were taken at various temperatures between room temperature and 300° C., and the data have been correlated with available data by other investigators.

The average coefficients of linear expansion for various temperature ranges between −250° and +300° C., as derived from the expansion curve in Figure 2 are as follows:

	$\times 10^{-6}$
−250° to + 20° C	25.1
−200° to 20° C	26.5
−100° to 20° C	28.3
+20° to 60° C	28.8
20° to 100° C	29.1
20° to 200° C	30.0
20° to 300° C	31.3

WASHINGTON, September 12, 1932.

[3] Souder and Hidnert, B. S. Sci. Paper No. 524 (fig. 11).